Development of an automated system for trace element analysis based on a novel flow digestion technique

Doctoral Thesis for the Doctorate of Technical Science

by

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Not with inventions, but with improvements one makes fortunes.

Henry Ford, 1863-1947

First of all, I would like to thank Dr. Friedrich Santner, General Manager of Anton Paar, to make it affordable to conduct this work parallel to my job as product manager. Special thanks are also going to my division manager, Peter Kettisch, as well as to all my other colleagues who had to deal with the fact of my reduced availability.

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1 Introduction

Modern sample preparation techniques for inorganic analysis mainly use wet digestions with mineral acids. Sophisticated instruments replace more and more classical hot plate and fusion techniques even for difficult matrices. These systems perform reactions in open and closed containers using microwave energy for fast heating. Computer controlled temperature and pressure profiles increase the reproducibility and handling safety.

Nevertheless, it is still necessary to fill the samples and reagents into the containers manually before the process and to transfer the final solutions to flasks after the process. Efforts to reduce this labour intensive task with the help of robotic systems or fluid handling devices have already been made. Difficulties with solid sample handling, insufficient performance and corrosion of the equipment by the acids used limited the success of such approaches.

This work describes the development of an automated flow digestion equipment based on a high pressure flow injection system and a conventional heated high temperature reactor. The aim was to improve existing sample preparation methods using batch processes, both conventional or microwave heated. All available existing systems need manual handling and manipulation to transform samples into a form applicable to modern analytical instruments. Using automation techniques for liquid handling, maintenance free sensors and a flexible control system should replace these tedious working steps. The aim was to built up a system that is able to run unattended for several hours up to one complete week.

2 Overview of flow digestion methods

The basic idea of replacing sample preparation batch processes with flow injection techniques is quite old. This section discusses the concepts, solutions and applications in the past. Only techniques used for trace element determination are covered. Other flow injection approaches, for example like clinical applications or decompositions running at temperatures of more than 600 ℃ normally are not covered in this section. This techniques are mainly used for total organic carbon measurement (TOC) or for phosphorous and sulfur determination

2.1 First flow digestion systems

The development of the first flow digestion system based on works done with continuous flow injection analysis setups. These techniques were used to produce high numbers of results for clinical applications running photochemical reactions or separations prior the determination. Continuous flow was first described by Skeggs [1, 2] in order to measure urine and blood samples. The sample and reagents were pumped with the help of peristaltic pumps, mixed with reagents and measured after passing through a reaction zone. Segmentation with air bubbles which were introduced in the continuous sample flow avoids mixing of the different sections within the tubing while internal mixing is remarkably improved. In most cases chromatographical determination methods were used, but there is already one paper from Lacy [3] of the year 1965 describing the coupling of a flame-AAS with a continuous flow system: only a few years after the first AAS systems were commercially available.

In the years 1972 and 1973 Sarbeck and Chuang [4,5] a group working together with Winefordener, described a sample introduction system which is nowadays known as the FIA system. But it took until 1975 and a paper from Ruzicka [6] to introduce the concept of flow injection analysis as a modification of the continuous flow technique. The determination of Mercury using the cold vapor technique is one of the successful examples of the coupling of flow techniques with measurement equipment.

The question for applicable material for connections and reactors was easy to answer: flexible tubing made of materials like glass or quartz were not applicable because capillaries made of this material have too small inner diameters to process interesting amounts of samples. Other material like Ni or porcelain, used for fusion techniques to determine major and minor compounds, is not suitable for trace elements. Glassware and quartz analysts have already used PTFE containers in traditional applications and for the growing number of microwave instruments at that time. Due to the high demand for ultra pure materials in semiconductor industry PTFE was available as tubes and hoses for flow reactions with limited contamination.

2.2 Heating techniques

When a proper reactor material was available, people had to answer the question of appropriate heating and cooling methods. As microwave heating was modern at that time and showed good results for pressurized applications, people did not like applying oil baths or heating blocks for these new approaches. Heating blocks made of metals are prone to contaminate samples due to the porosity of PTFE tubing, oil baths are not very comfortable and safe in handling. Therefore almost all papers dealing with flow digestion described the use of different microwave systems to heat the samples. Only few approaches use conventional heating blocks or resistant heating elements.

2.2.1 Multimode microwave applications

The first system using microwave heating in combination with a flow system was described by M. Burguera and J.L. Buguera [7] in 1986. They still used a glass tube installed in a simple kitchen microwave oven with two holes drilled into the cavity instead of a PTFE. Two peristaltic pumps transported sample whole blood and acid and mixed them inside the heated tube in the oven prior/before the reaction. On the other side the solution was directly transported to a flame-AAS for transient Copper, Zinc and Iron measurement.

Two years later the same authors [8] described a system which automatically mixed samples and acids and filled them into six digestion containers within a kitchen microwave oven. After the reaction the solutions were removed by suction and a small portion of it was tested for Zinc and Cadmium. The materials used for the experiments were solid biological reference materials (NBS bovine liver SRM 1577 and oyster tissue SRM 1566) which showed good recoveries.

In 1990 a PTFE hose reactor was used to determine phosphorous in water and waste water. In order to prevent too much dispersion within the tubing which was installed at the walls of a kitchen microwave oven, the hose was knotted. The group around Hinkamp [9] tested the system with various organic and inorganic phosphorous containing materials.

Another system used for the determination of phosphates in waste water was described by R.L. Benson [10] and his team. For the first time a temperature and pressure measurement was installed at the end of the system via a t-piece. As electronic measurement inside the kitchen microwave oven was difficult, the sensor was installed outside the cavity. The determination was carried out using a photometric method.

The system described by Carbonell [11] et al., a group working with Burguera, used cooling air slits of a microwave oven to enter the cavity with a PTFE hose. The reactor decomposed materials like food or sewage sludge after having it dispersed in concentrated nitric acid in a glass container using a magnetic stirrer. First a method optimized for Pb was described, later the technique was also used for Copper and Manganese. A mixture of HNO_3 and H_2O_2 efficiently extracted these three elements from the samples at the applied conditions.

In 1993 M. Burguera and J.L. Burguera [12] also used a PTFE hose as reactor, again installed in a domestic microwave oven. The system was connected online to an autosampler of an ETV-AAS to determine Pb in biological materials. For gas separation a special PTFE diffusion cell was developed to remove the gaseous by-products of the digestion. The solid sample materials were suspended in concentrated nitric acid with the help of an ultrasonic bath and stabilized by detergents. Later the group used this system for direct determination of Copper, Zinc [13] and Cobalt [14] in whole blood received directly from veins.

Haswell and Barclay [15] investigated improvements in digestion quality due to higher temperature within the reaction system by increasing the working pressure. The pressure in the FIA system was built up with the help of a HPLC pump and regulated by an electronic backpressure valve at the end of the reactor and cooling system. Their design ideas were finalized with the production of a commercial product, the SpectroPrep from the American company CEM (see chapter 2.3.1).

2.2.2 Low-pressure monomode microwave applications

Parallel to the works done with multimode microwave ovens other groups used another popular laboratory microwave system from Prolabo, the MaxiDigest. This system applied focused microwave energy within a microwave guide which allowed for sufficient heating with less energy. The small cavity (inner diameter 48 mm, height 32 mm) was used to install PTFE coils, knotted tubes or borosilicate reactors.

A group working with Tsalev [16, 17] combined a PTFE tubular digestion reactor within the focused microwave system and a commercial FIAS 200 system from Perkin Elmer to determine Hg, As, Bi, Pb and Zn in urine and water samples. Guo and Baasner [18] had a similar setup for mercury determination in blood samples using a 10 m PTFE tubing for longer retention time leading to better digestion results. The reactor was knotted to minimize the dispersion due to the long tubing. Several other configurations were used to digest biological materials or waste water for determinations of different elements using a flow injection mercury system FIMS [19], CV-AFS [20], ICP-MS [21] or ETV-AAS [22].

To apply acids with higher boiling points like sulfuric acid borosilicate reactors replaced PTFE coils [23] to improve the decomposition performance due to higher temperatures. Solutions of whole blood, milk and urine were analyzed by ICP-OES after digestion.

To avoid the disadvantages of sulfuric acid like impurity and high viscosity Welz et al. [24] applied a restrictor at the end of the PTFE tube to increase the temperature. The pressure increase of 6 bar increases the boiling point of nitric acid to approximately 150℃. This leads to better decomposition effects and also reduces the formation of bubbles during the process. The setup was applied for the determination of arsenic using the hydride formation technique.

2.2.3 High pressure monomode applications

A completely different setup compared to the oven systems described above used a non commercial monomode waveguide to run high pressure applications up to 35 bar. The group around Knapp and Michaelis transferred the basic principle of the High Pressure Asher from Knapp [25] to flow digestion systems. The limitation of all other systems at that time was the low maximum working pressure due to the weakness of the tubings used. Knapp overcame this problem by applying high pressure via an external nitrogen tank into a pressure capsule containing the reaction coil. The capsule was made of a microwave transparent material like PEEK or ceramics located inside a microwave waveguide. With the help of this design the tube was supported from outside against the reaction pressure from inside the hose. The only limitation of the configuration was the temperature stability of the tubings used. The supporting pressure also set the internal pressure as the coils open end pointed into the pressurized cell. A collection tubing, which had a larger inner diameter than the reaction tube, guided the sample solutions to a collection vial via a restrictor tubing. With the help of this design no backpressure regulator was needed against the HPLC pump to control reaction conditions. In case of enough microwave power the pressure regulated via the set boiling point also the maximum temperature inside the system. The solution and the supporting nitrogen gas were released from the pressure capsule via the restrictor, a PTFE tube with a certain length to adjust the backpressure (see Fig. 2 - 1). The setup was used to digest biological standard reference materials for the determination of various elements via ICP-OES and ET-AAS [26]. A syringe pump took acid plugs before and after the sample plug and loaded the sample into the injection loop. Compared to other microwave systems, this design was able to run very efficient decomposition due to its high performance. Nevertheless, limited success of other commercial microwave systems at that time prevented the market introduction of the system described.

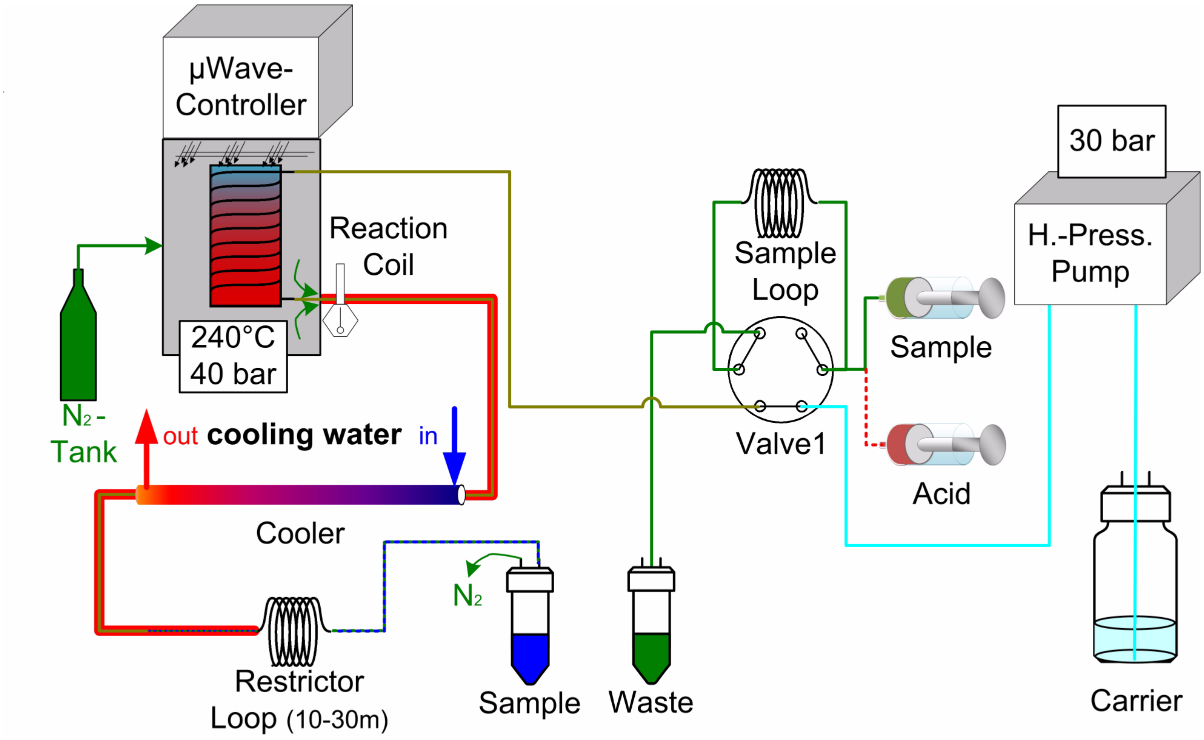


Fig. 2 - 1 Working principle of the autoflow digestion system

2.2.4 Conventionally heated flow digestion systems

Although many papers deal with microwave heated systems, only few reports are made for systems using conventional heating via heating blocks or resistant heating techniques. Tyson described a PTFE coil wrapped around a heating block in an insulated reaction chamber to digest biological materials for Copper and Iron determination [27]. Due to problems with limited digestion temperature, the performance was weak, therefore Tyson modified the system to apply microwave heating in a laboratory microwave system using a borosilicate reaction coil [28]. Berndt described a conventional system [29] using a Pt-Ir capillary as reactor material instead of PTFE tubings which allowed extremely high temperatures and pressure to digest biological materials. He combined the system with a degassing unit and spray nozzle to couple it directly to AAS or ICP systems. Based on his ideas, the new automated online analysis system, which will be described later, was developed.

2.3 Commercial flow digestion systems

2.3.1 Continuous flow systems

The first commercially available flow digestion system was the SpectroPrep from CEM, Matthews, USA based on works done by Haswell and Barclay [15]. It allowed automated flow digestion using two autosamplers, one for sample input and one for collection of processed solutions. The reactor coil consisted of a 30 m long PTFE tubing with Kevlar reinforcement within a special microwave unit instead of standard laboratory or kitchen equipment. A HPLC pump built-up the pressure inside the system against a pressure regulation valve adjusted by the build-in microcontroller. With the help of the reinforcement pressure ratings of up to 25 bar could be reached. The higher pressure increased also the reaction temperature up to 200℃ using HNO_3 or Aqua Regia. The higher temperature increased the performance compared to the academic systems described before. The sample was injected with the help of a high pressure injection valve. Another high pressure valve at the end of the system guided the samples through a filter prior collection or allowed backflush of the filter after finalizing the digestion.
Gas bubble formation inside the tubing during the process caused micro-separation of the sample which limited dispersion during the process.

It was reported [30] that too high organic loads in the sample caused high pressure built-up by forming gaseous reaction products. This overpressure opened the regulation valve. The sample was released faster than when transported with the HPLC pump only. Faster flow meant also a shorter retention time and therefore a lower digestion quality. Another problem of the setup was the limited maximum slurry concentration. Higher concentrated slurries often caused blockades of the system due to the fast release action of the valve. Undissolved sample material exited the system and clogged the tubings or the filter. The systems ability to handle maximally 1% w/v inorganic slurries and even lower amounts for biological materials restricted the applicable types of samples that could be analyzed. Only the use of the most sensitive elemental detection devices such as ICP-MS allowed to get acceptable detection limits. Sales of the system stopped approximately 2 years after its introduction due to limited technical and economic success. Using the SciFinder index only 2 international and 2 german publications could be found which indicates its limited number of applications. In comparison, between minimum 10 to 40 papers describing the use of the batch system can be found for the three main microwave digestion systems producers (CEM, Milestone and Anton Paar).

The publication by Mason [30] describes the modification of the SpectroPrep system to overcome limitations known for real samples. One was the very likely failure of blocking the back-pressure regulator by undissolved sample material. Another problem occurred when the organic content in the sample was too high, causing too fast pressure build-up. In such a case the opening of the safety port released the sample without reaction. One important modification was the replacement of the standard injection valve with a valve offering an inner port channel of 1.5 mm to avoid blockades at that position. Mason also replaced the electronically controlled back-pressure regulator with a peristaltic pump which used pump tubes with Kevlar armor from the standard reaction tube of the SpectroPrep to increase the working pressure. Using this configuration the maximum pressure was 16 bar, the external measured temperature at the tubing was 116 ℃. Taking a pressure of 16 bar steam tables more likely indicate temperatures around 170 to 180 ℃ using concentrated HNO_3. The difference could be attributed to lacking contact between the temperature sensor and the tubing. PTFE is known for bad heat transport through the tubing showing much less temperature on the surface than inside the tubing.

2.3.2 Stopped flow systems

Another commercial system on the market was produced by the company Questron and is called AutoPrep. Instead of the continuous process stream a stopped flow procedure was used, which was first described by Karanassios [31] and was used to digest samples in a microwave reactor. Due to its design, a high pressure pump was not necessary. The sample and acid were pumped into the system using a low pressure pump. Pressure resistant valves in front and at the end of the reactor closed the system prior microwave heating. The microwave power was adjusted to avoid a pressure higher than 8.7 bar. After finishing the heating, the outlet valve opened and released the sample. The relatively low process pressure and thereby low reaction temperature led to undissolved material, which is why additional filtration was necessary. This system had a similar short lifetime on the analytical markets due to its performance limitations. Searching via Science Index, no publication could be found which indicates its minimal importance for the routine or scientific work.

3 Conventional heated flow digestion system with noble metal capillaries

As shown in the overview section, flow digestion was a hot topic between 1986 and approximately 2000 with many publications. During that time mainly microwave heated systems and two main commercial systems were discussed in publications. There was only one group around Berndt using traditional resistant heating for a modern flow technique. Berndt discovered that it is absolutely unnecessary to use complicated and more expensive microwave generators that need a constant reagent flow at constant temperature and pressure. The advantages of modern laboratory microwave equipment are fast heating and cooling of containers. For high performance flow digestion at extreme temperatures, these changes in temperature are neither necessary nor wanted. Using conductive heating instead of microwaves, non microwave transparent materials like metals can be used to overcome the thermal and mechanical limitations of PTFE tubings or reinforced polymer materials.

3.1 Basic considerations

The basic configurations for all flow digestion systems did not vary remarkably. The low pressure systems used peristaltic pumps to transport samples and reagents, for high pressure applications HPLC pumps were used to build up the necessary system pressure. The exception to this rule was the stopped flow configuration from Karanassios. This system built-up pressure by heating the samples in the reaction loop after closing it hermetically with pressure resistant valves [31].

One problem all systems faced is the fact that flow injection of a sample-acid-mixture into a stream of diluted acid or water as carrier can cause bad digestion results. The oxidizing acid on both ends of the sample-acid plug gets diluted which led to reduced decomposition results. Advanced setups from Knapp and Berndt [26, 32] therefore nested the acid-sample-mixtures between concentrated acid plugs to avoid dilution by the carrier. In Fig. 3 - 1 the typical load pattern of such a system can be seen. Mason and his group only pre-loaded oxidizing reagents in front of the sample-acid-mixture. This setup was able to showing similar positive effects concerning the digestion efficiency compared to standard flow injection approaches [30].

Fig. 3 - 1 Nested sample-acid-mixture to avoid dilution of oxidizing reagents

Following the principles of Knapp and Berndt all different setups during the development of the new flow digestion system used the additional acid plugs to increase the digestion performance.

3.2 Instrumental configuration for high pressure flow digestion

For his investigations [33] of different capillary systems Berndt used a flow setup with only one injection valve before the reaction coil. The installation of a second valve [32] allowed him injection of the sample guarded with two concentrated acid plugs as described in chapter 3.1.

Fig. 3 - 2 shows a detailed flow chart with a HPLC pump for pressure build-up, a sample introduction system consisting of two high pressure injection valves, a heated reaction capillary with insulation as well as an air cooler in front of a Polysil or PEEKsil restrictor capillary. In brackets an alternative tubing material with indirect heating (using a resistant wire coil) can be seen. This technique replaced, for example, metal capillaries which are heated by applying electrical cables directly on the tube using the capillary itself as resistive heater.

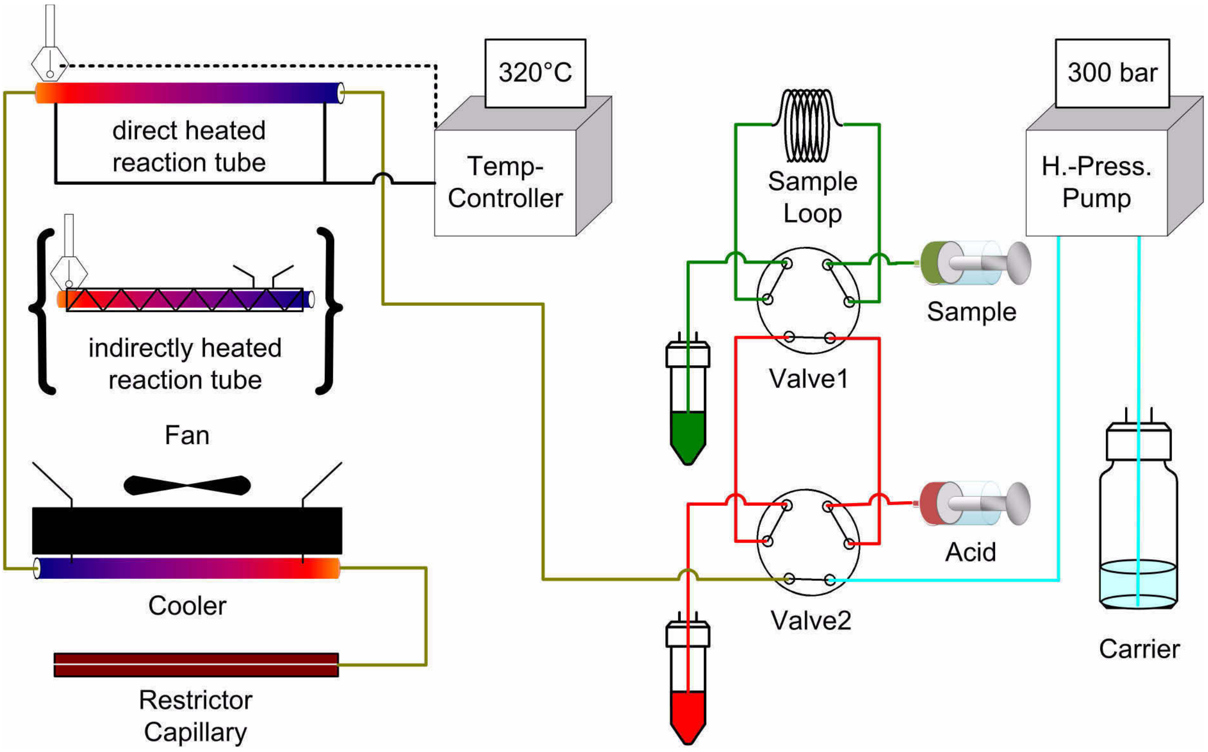


Fig. 3 - 2 Directly heated Pt-Ir-tube high temperature and pressure digestion system

The high pressure pump used water to build up pressure within the system. Two connected high pressure injection valves (Valve 1, Valve 2) allowed the injection of a sample volume defined by a sample loop on valve 1. The size of the acid plugs in front and after the sample/acid mixture is defined by the tubing lengths between valve 1 and valve 2 and can not be varied from sample to sample.

For such a configuration it is necessary to mix the sample with acid before loading it into the loop in valve 1. First sample preparation trials were made with different capillary materials, wrapped with heating wires for the quartz capillaries. The metal capillaries were directly conducted with wires to a temperature controlled power supply. The capillaries were coiled to save space and to make their insulation in the high temperature reactors easier.

The temperature sensor was installed at the end of the tube or in the middle of the capillary. Finally, Berndt used a heated aluminum cylinder to wrap the metal capillaries around and fixed them with a sleeve. This design pressed the reaction coil intensively to the central electrically heated cylinder for good heat transfer.

3.2.1 High pressure noble metal reactor with restrictor capillary

The reactor consisted of a Pt-Ir - capillary (80/20) with 1/8" OD, 1.0 mm ID and a length of 1500 mm. Only 1000 mm of the capillary were heated by wrapping the tube around an electrically heated aluminium cylinder with a diameter and height of 50 mm. The heating block was powered by a 42 volt and 250 watt heating element. The coil was fixed by two metal clamps to guaranty proper heat transfer between the aluminium and the capillary. The heating block was covered by isolating material and an additional metal shield around the isolation to form the oven. The remaining part of the capillary was fixed between two copper plates, each 60 mm x 80 mm with a milled groove to take the capillary. On the copper plates a cooler, which is normally used as CPU cooler in personal PC's with fins and a fan, cooled the passing medium down from more than 300℃ to less then 40℃.

A homemade temperature controller regulated the system's temperature. A HPLC pump with a titanium head (Knauer 64, Berlin, Germany) was used to build up the reaction pressure. Different lengths of restrictor capillaries (ID = 64µm, OD = 1/16", Upchurch Scientific, Oak Harbor, WA) at the end of the reaction capillary adjusted the system's working pressure according to the chosen flow rate. It was not possible to adjust a new flow rate without changing the pressure. To maintain a certain pressure at different flow rates a change of the capillaries were necessary. Typical pressure values at different lengths and pump rates can be seen in the following Table 3.1.

Table 3.1: Pressure values for different flow rates and restrictor capillary lengths

Flow rate [mL/min]	Capillary Length [mm]	System Pressure [bar]	Capillary Length [mm]	System Pressure [bar]
0.4	1040	112	1270	124
0.6	490	114	700	121
1.0	490	136	700	183
1.2	380	119	490	160

The scheme of the setup can be seen in Fig. 3 - 3. The figure is taken from Berndt's publication [32] showing the coupling of the system with an ICP-system.

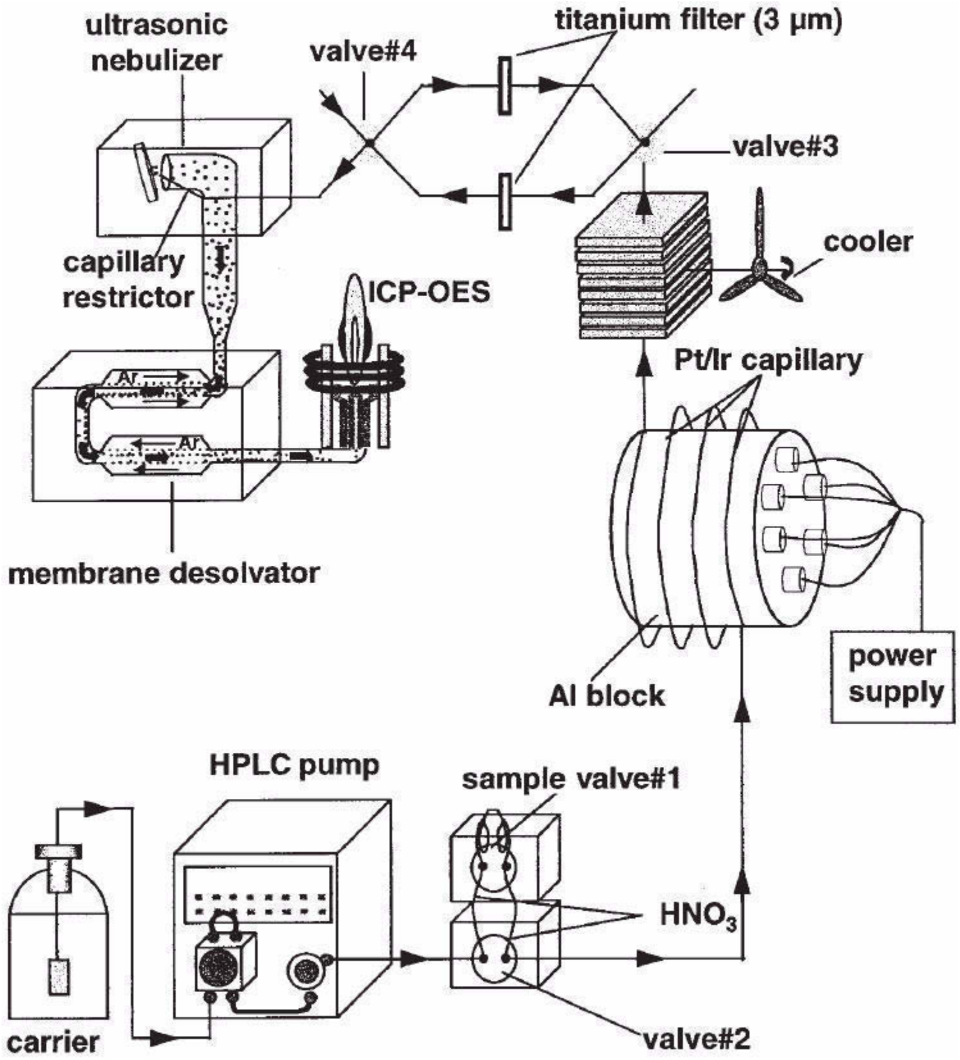


Fig. 3 - 3 High performance digestion system using a conventional heated Pt-Ir-capillary

The digestion part from Fig. 3 - 3 can be seen as laboratory setup in Fig. 3 - 4. The system was build up on a laboratory cart, a magnetic stirrer was used to mix the sample/acid slurry before the injection into the sample loop. Two manual high pressure injection valves (1/8'', PEEK, Knauer Berlin, Germany) were connected by 1/8'' PEEK tubing. The same material was used for the sample loop. The loop had a volume of typically 0.5 mL, the two connection tubes between the two valves had 0.65 mL. Two syringes, each connected to a three-way valve allowed loading of the sample and the acid loop.

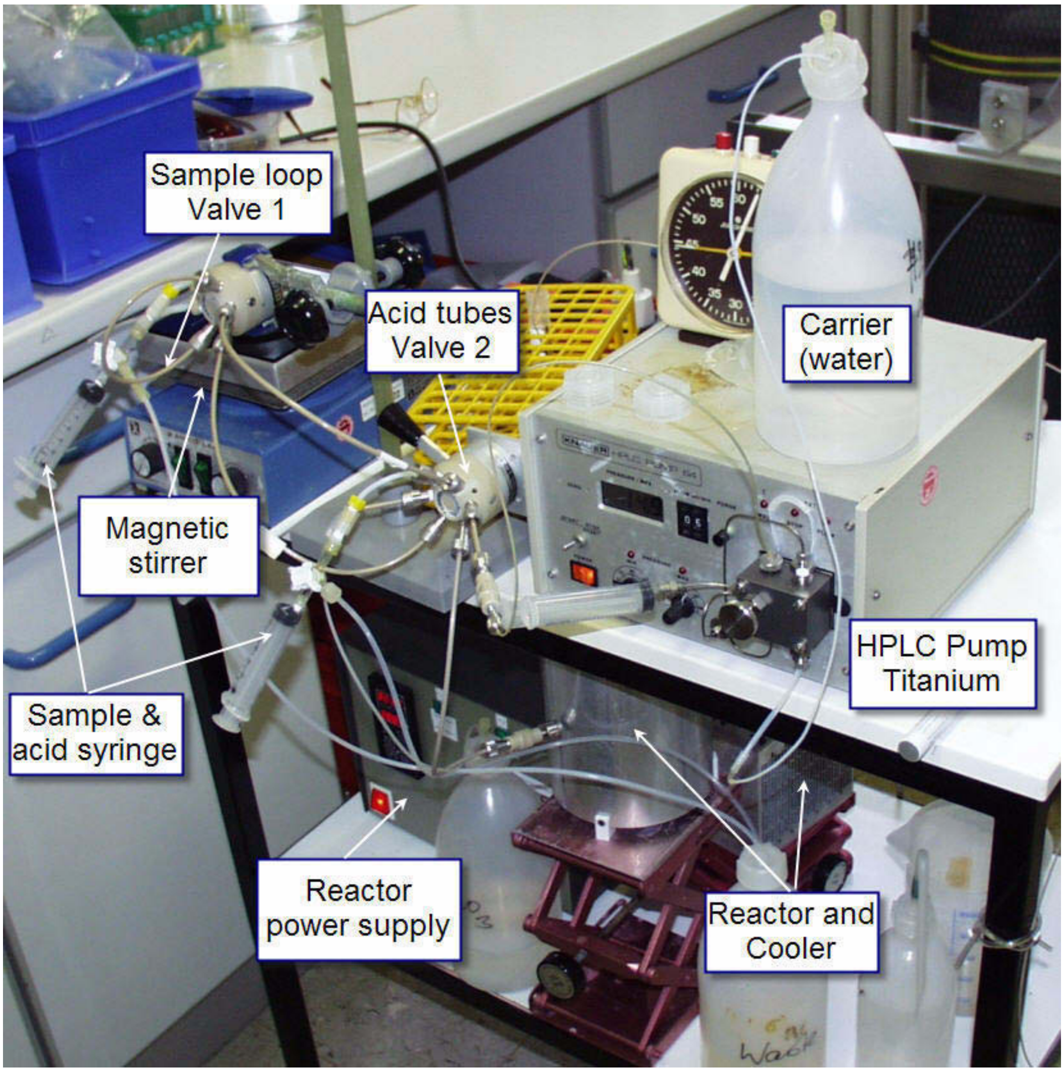


Fig. 3 - 4 Laboratory setup of Berndt's flow digestion system with a Pt-Ir-capillary

The stop watch was used to determine the collection start after manual injection. The end of the collection was defined by the chosen collection volume measured with the help of a graduated vial.

3.2.2 Microwave heated flow system with a pressure supported PTFE-capillary

The system described in chapter 3.2.1 was compared with the microwave flow digestion system of Knapp [26] using the same samples. For this tests a configuration with a manually loaded sample loop was used. In Fig. 3 - 5 the schematic configuration can be seen. The reactor coil, consisting of a 32 m PTFE hose (i.d. 1.0 mm; o.d. 1.6 mm), was located in the pressurized autoclave. The sample cooler consisted of a PEEK supported PTFE tubing inside a water cooling hose which was made of silicon. A restrictor hose (i.d. 0.5 mm; o.d. 1.6 mm, 18 m) reduced the internal pressure from 40 bar to ambient pressure. A HPLC pump transported the carrier and maintained the flow against the set pressure from the nitrogen tank supplying the reactor chamber.

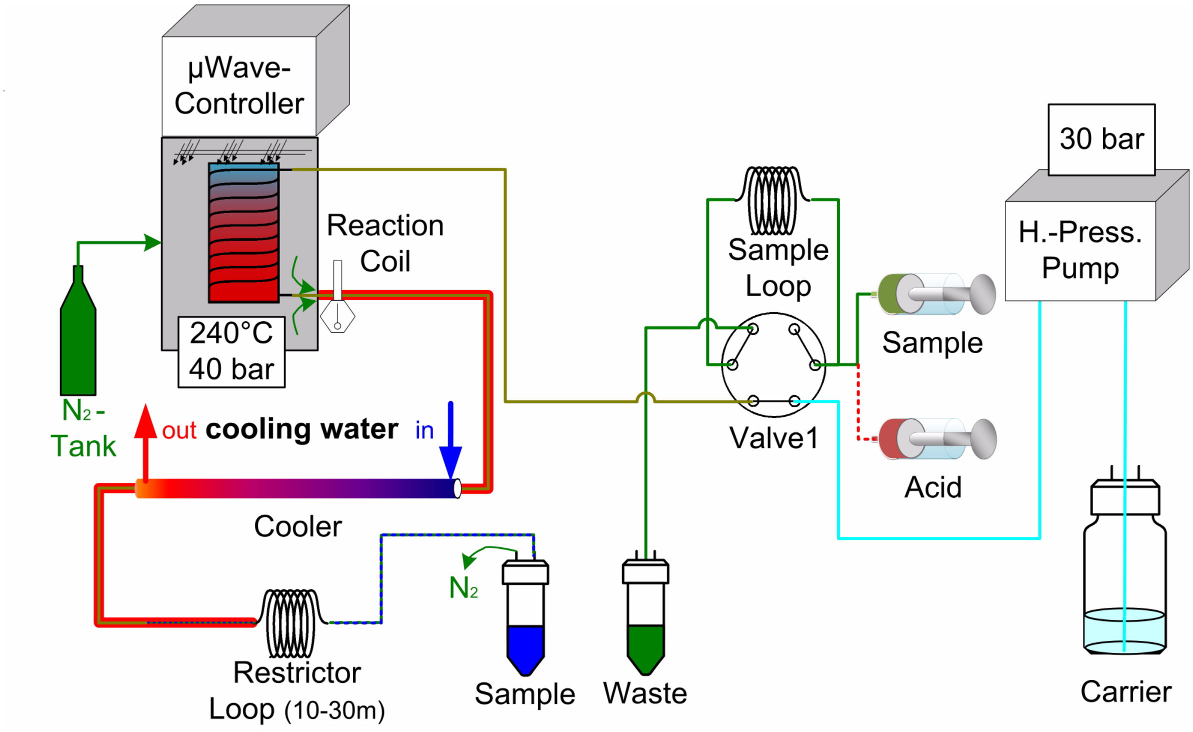


Fig. 3 - 5 Flow chart microwave digestion system with manual loading

The laboratory setup with a specially designed focused microwave autoclave and a manually switched valve can be seen Fig. 3 - 6. The sample and the restrictor loops are mounted together with the injection valve in a protection box. The reactor outlet with cooler tubing connects the microwave autoclave with the restrictor in the safety box. Beside the microwave system the HPLC-pump can be seen.

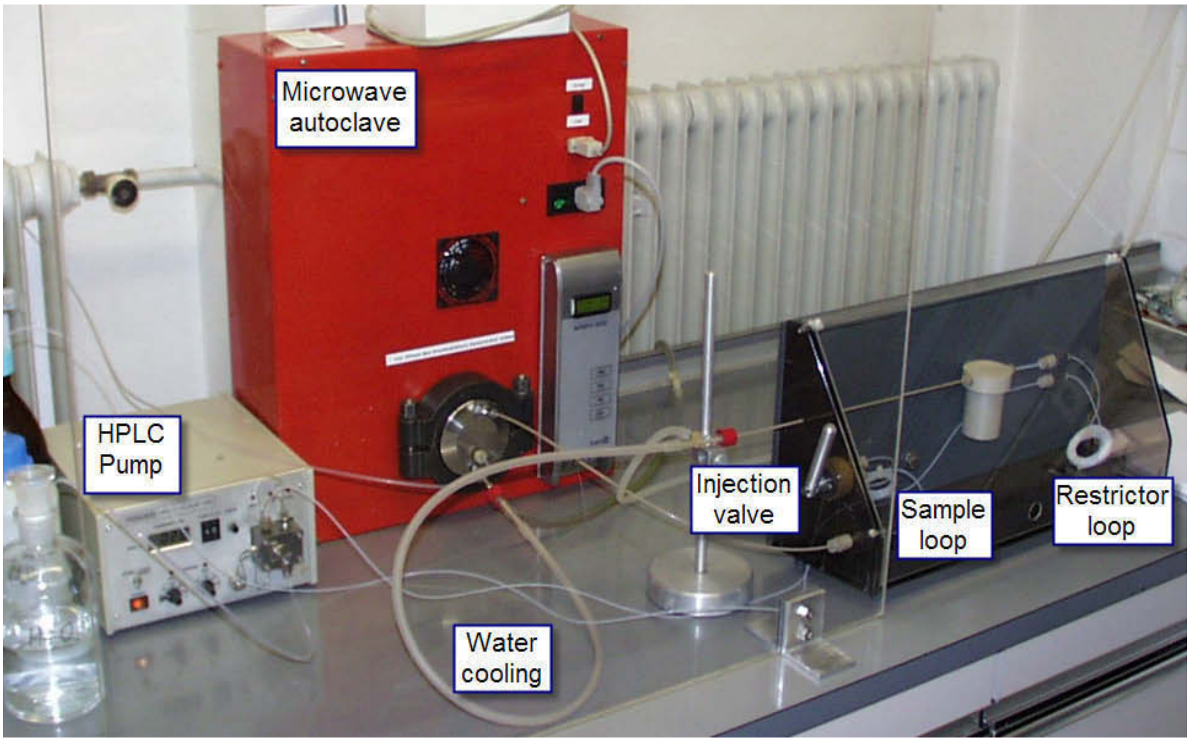


Fig. 3 - 6 Test setup with focused microwave autoclave and water cooled PTFE coil reactor

3.3 First performance verification experiments

For performance comparison experiments Berndt brought his system (chapter 3.2.1) to Graz where it run comparison experiments against the microwave heated flow digestion setup of Knapp (chapter 3.2.2) and a commercial high performance microwave batch digestion system. The goal was to determine the possibilities of a simple setup as described above compared to the more complex configuration of Knapp's high performance microwave flow system which needed additional pressure and cooling water supply.

For the experiments nitric acid (2.5 M) was used to fill the sample loop on valve 2 and to allow a nested injection of the sample into the reactor. The sample slurries, also prepared with 2.5 M nitric acid, were made from carefully mixed and homogenized food samples similar to the methods described by Haase and Pichler [26].

Table 3.2: List of sample slurries applied in the experiments:

Sample	**Weight**	**Reagent** (high pressure system)	**Reagent** (µ-wave system)
Lettuce	1.6 g	12 mL 2.5 M HNO_3	12 mL 5 M HNO_3
Apple	1.0 g	12 mL 2.5 M HNO_3	12 mL 5 M HNO_3
Ham sausage	0.4 g	12 mL 2.5 M HNO_3	12 mL 5 M HNO_3
Liver pâté	0.2 g	12 mL 2.5 M HNO_3	12 mL 5 M HNO_3

The carefully mixed and weighted sample materials (mixer with titanium blades, Buechi) were covered with the acid mixture shown in the table and homogenized only a short time before the digestion for 3 min using a titanium ultra turrax mixer. While sampling from the container with a syringe, a magnetic stirrer was used to avoid precipitation of the sample materials.

The typical sample concentration in the slurries applied by Berndt in earlier experiments was between 0.1 and maximally 4 %. To reach better detection limits and higher reproducibility with the applied sample volume, higher concentrated slurries (1.0 to 10 %) were prepared for the experiments (see Table 3.2). These slurries have previously been used by the group working of Knapp for their microwave flow digestion system [26] and should allow a good comparison of the two different methods.

3.3.1 Recovery tests with the nobel metal capillary flow system

Experiment:

After the system had been heated up with water, two blank digestions with acid (2.5 M nitric acid) were done to clean the system before the first digestions. First a recovery test had been done with a glucose solution [1 %] containing 100 µg/g Mn. For this test the digested solution was collected in 0.8 mL fractions. The digestion solutions were collected by guiding the end of the restrictor capillary into a collection vial. The start point for collection is dependent on the pump rate of the experiment and the actual size of the reactor. The end point was determined by reaching a certain collection volume measured by means of the graduated collection vials.

Mobile phase:	water
Sample:	0.5 mL (1 - 10 % slurry with 2.5 M HNO_3), nested between 2 x 0.65 mL with 2.5 M HNO_3 or 1.0 mL after modification of the configuration

Collection Volume: 5 mL

Flow rate: 0.4, 0.5 or 1.2 mL/min; retention time within the reactor: 90, 80 and 30 s

Temperature: 320 °C

Pressure: 113 - 176 bar

Recovery tests:

0.8 mL collected sample were filled up to 2 mL and measured by F-AAS (PE 5000, Perkin Elmer, Shelton, USA)

Table 3.3: Recovery test comparison Autoflow against Pt-Ir-capillary system

Time [min]	**Mn [µg/g]**
0 - 2	0.0
2 - 4	0.0
4 - 6	14.2
6 - 8	28.0
8 - 10	8.8
10 - 12	0.4
	51.4

Mn-recovery: 102.8%

3.3.2 Recovery tests with a microwave heated PTFE-flow system

Experiment:

After start up of the Autoflow microwave system (chapter 3.2.2) each sample was treated three times. Two syringes were used to fill the sample loop with acid-plugs and the sample slurry. The following digestion procedures were used:

Mobile phase: HNO_3 20 mL/L water

Sample: 3.0 mL (1 - 10 % slurry with 5 M HNO_3), nested between 2 x 1.0 mL 5 M HNO_3

Collection Volume: 10 mL

Flow rate: 5.0 mL/min

Temperature: 240 °C

Pressure: 40 bar

Four minutes after manual injection, the collection of the sample started by directing the end of the restrictor capillary into a vial. After two minutes the collection stopped, reaching the target volume of 10 mL. The results are shown in chapter 3.3.4.

3.3.3 Recovery tests with a microwave heated batch digestion system

In addition to the experiments with the described flow systems, the same materials were also prepared with a microwave batch digestion system (Multiwave with 50 mL quartz vessels, Anton Paar, Graz, Austria) to compare the results with an established procedure.

For the closed vessel microwave digestion, the mixed acified samples were applied directly into the quartz reaction containers (50 mL) and each was covered with 4 mL concentrated nitric acid (subboiling: 65%).

Closed vessel microwave procedure:

All quartz reaction containers were pressure and temperature controlled. The maximum reaction pressure was set to 72 bar, the corresponding temperature was 240 °C.

Table 3.4: Digestion Program:

Power	Time	Power	Fan
1000 W	25 min	1000 W	Fan 1
0 W	15 min	0 W	Fan 2

Sample weight:

Apple, lettuce	2.0 g
Sausage, pâté	0.5 g

After cooling, the reaction vapors were released and the solutions transferred to graduated flasks. Before determination, the samples were transferred to autosampler vials and filled up to 20 mL using the rinsing solutions of the reaction containers.

3.3.4 Results for the comparison of flow and batch procedures

The collected samples were measured for trace elements using an ICP-OES (Optima 3000 XL, Perkin Elmer, Shelton) and for remaining organic compounds via a TOC Analyzer (TOC-5050 A, SHIMADZU, Duisburg). The remaining organic carbon concentration has been shown to be a very good indicator of the quality of the digestion process[35, 36, 37, 38], therefore the results should help to rate the digestion efficiency of the three tested systems.

Table 3.5: Comparison for an apple slurry digestion using 3 different digestion techniques

	AutoFlow	**Pt-Ir system**	**Multiwave**
Apples	Mean ± SD µg / g	Mean ± SD µg / g	Mean ± SD µg / g
Ca	36.5 ± 7.5	46.0 ± 2.7	44.0 ± 6.8
Cu	1.08 ± 0.50	1.07 ± 0.07	-
Fe	8.14 ± 5.9	2.43 ± 1.41	0.98 ± 0.05
Mg	52.9 ± 1.2	59.0 ± 1.0	65.9 ± 0.6
Mn	0.40 ± 0.06	0.44 ± 0.01	0.64 ± 0.01
Zn	2.58 ± 0.70	3.50 ± 0.46	0.67 ± 0.07
TOC [%]	0.38 ± 0.04	0.48 ± 0.07	0.06 ± 0.03

Table 3.6: Comparison for a lettuce slurry digestion using 3 different digestion techniques

	AutoFlow	**Pt-Ir system**	**Multiwave**
Lettuce	Mean ± SD µg / g	Mean ± SD µg / g	Mean ± SD µg / g
Ca	364 ± 28	448 ± 4	536 ± 13
Cu	0.45 ± 0.07	0.50 ± 0.04	-
Fe	15.2 ± 2.3	9.94 ± 0.66	25.2 ± 1.6
Mg	115 ± 8	140 ± 2	172 ± 3
Mn	2.17 ± 0.15	2.60 ± 0.05	3.22 ± 0.06
Sr	0.99 ± 0.07	1.26 ± 0.01	-
Zn	1.10 ± 0.01	2.10 ± 0.28	1.22 ± 0.06
TOC [%]	0.41 ± 0.03	0.24 ± 0.04	0.06 ± 0.02

Table 3.7: Comparison for a sausage slurry digestion using 3 different digestion techniques

	AutoFlow	**Pt-Ir system**	**Multiwave**
Sausage	Mean ± SD µg / g	Mean ± SD µg / g	Mean ± SD µg / g
Ca	34.1 ± 0.70	61.0 ± 4.2	97.2 ± 2.0
Fe	5.36 ± 1.00	27.8 ± 1.1	7.48 ± 0.14
Mg	79.9 ± 1.0	109 ± 1	202 ± 71
Zn	7.26 ± 0.10	12.2 ± 0.64	19.2 ± 3.4
TOC [%]	2.70 ± 0.10	0.61 ± 0.04	0.24 ± 0.05

Table 3.8: Comparison for a pâté slurry digestion using 3 different digestion techniques

	AutoFlow	**Pt-Ir system**	**Multiwave**
pâté	Mean ± SD µg / g	Mean ± SD µg / g	Mean ± SD µg / g
Ca	243 ± 5	251 ± 8	114 ± 21
Cu	11.8 ± 0.1	17.2 ± 0.8	-
Fe	89.0 ± 2.3	124 ± 51	36.9 ± 25.0
Mg	172 ± 3	170 ± 5	152 ± 68
Mn	2.60 ± 0.08	2.57 ± 0.74	-
Zn	37.2 ± 0.7	49.7 ± 0.6	20.7 ± 3.1
TOC [%]	18.5 ± 1.5	3.50 ± 0.90	0.77 ± 0.14

Discussion:

The comparison of the three different digestion techniques for four matrices shows the differences in digestion quality. The TOC level was always the best for the microwave batch system while the Pt-Ir system was second, except for the apple sample. The main reason is the possibility to release the formed reaction gases into the empty container space above the sample in the batch container; a possibility missing for both flow systems. Another interesting point was the generally lower standard deviation for the batch system due to the higher sample amount and lower dilution factors. The measured element concentrations are on one hand partially comparable between the flow systems as can be seen for Cu, Mg and Mn for the apple sample. Other elements on the other hand are showing large variations like for Fe in the pâté sample. The use of the ultra turrax mixer could not completely solve the homogeneity problem caused by the limited sample amount. The poor decomposition quality added negative effects for the element determination. Only for Mg the results were in the same magnitude for all three techniques except for the sausage sample. Largest variations could be seen for Zn in all samples. These poor results were the reason to develop a new system capable to decompose more material to improve the analytical results.

3.4 Design-improvements for the capillary flow digestion system

3.4.1 Sample load limitations of the basic setup

After digestion of the samples for the comparison experiments, higher concentrated slurries (10-20 %) were tested with Berndt's setup. For that higher concentration level the system failed several times after injection of the slurries. The sample loop slipped out of the fitting on the injection valve due to the system's fast increase of reaction pressure. In such a case the whole content of the reactor vented within few seconds as water and acid vapor. After resealing with higher torque of the fittings and running through the complete heat-up procedure, the same samples were tested again, leading to similar problems. As the loop was made of a 1/8" PEEK tube, the limited pressure stability of 1/8" fittings was suspected to be the main source of the troubles after injection. The used flat bottom flangeless fittings are designed for a maximum working pressure of 200 bar. Further experiments should use 1/16" tubings and fittings to offer higher pressure stability of 375 to 500 bar depending on the thickness of the used tubing's wall.

3.4.2 Design improvements for the noble metal capillary system

Berndt's flow reactor test system was only available for 2 testing days, therefore it was necessary to design and build up another test-equipment for further investigations. The modified setup should offer operation with different versions of digestion capillaries and only one injection valve. The advantages of this setup compared to the basic concept with two valves were the free adjustable acid plug size, the easier automation and lower costs.

The newly designed setup was based on Berndt's original concept. The goal for improvement was to miniaturize the components and combine them in one single case including reactor, cooler and temperature controller. Only the sample and acid handling were still separated to use the existing liquid handling setup of the microwave flow digestion system available at the institute.

For the reactor, the proven aluminium heating block with sleeves was used to heat 1.0 m of the 1.5 m long, Pt-Ir-capillary (80% Pt, 20% Ir, 1.6 mm o.d., 1.0 mm i.d.; DEGUSSA, Hanau, Germany). To gain higher chemical resistance, especially for methods needing higher levels of HCl or containing chloride, a capillary with a higher Ir-level was needed, but not available. The capillary in use offered the highest Ir-level still allowing the seamless drawing of tubes. Higher Ir concentrations cause higher brittleness which leads to drastically shorter tubings if drawing is possible at all. Other 1.6 mm Pt-Ir-tubings (ÖGUSSA, Vienna, Austria) tested by Berndt were welded, showing hair cracks even at relatively low temperature and pressure.

The isolation was done with several layers of a glass wool fabric (Merck, Darmstadt, Germany) and fixed with a high performance adhesive film for thermal isolation applications. The 100 W, 230 V heating element was regulated by the µ-processor controlled digital temperature regulator KS-20-I (PMA, Kassel, Germany) and triggered with the help of a solid state relay (Crydom, San Diego, USA).
For temperature control a Pt100 sensor (Correge, Chaignes, France) was used to measure the temperature of the heating block at a position between the heating cartridge and the capillary.

For fast cooling 100 mm of the capillary were mounted between two aluminium heat sinks (Assmann, Austria) and additionally cooled with the help of a cooling fan (EBM-Papst, Mulfingen, Germany), providing typically 30 m^3/h cooling air through the case, also cooling the controller and the reactor itself. The Pt-Ir-capillary was mounted to the injection valve with the help of 1/16" PEEK SealThight Fittings (Upchurch, Oak Harbor, USA). To connect the PEEK restrictor capillaries (see Table 3.1) to the Pt-Ir capillary, a PEEK union 1/16" 10-32 conical and again two 1/16" PEEK SealThight Fittings (both Upchurch, Oak Harbor) were used.

The system case was made of a 1.5 mm stainless steel sheet metal by laser cutting and welding. The assembled system is shown in Fig. 3 - 7 and without the protection case in Fig. 3 - 8.

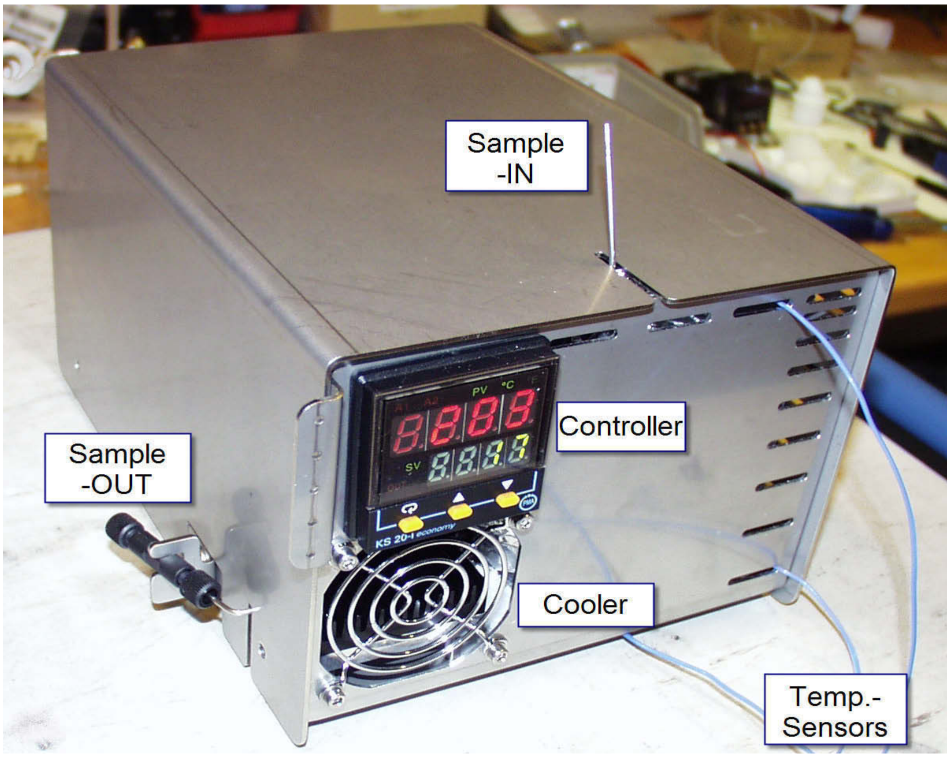


Fig. 3 - 7 Pt-Ir-reactor, new compact design

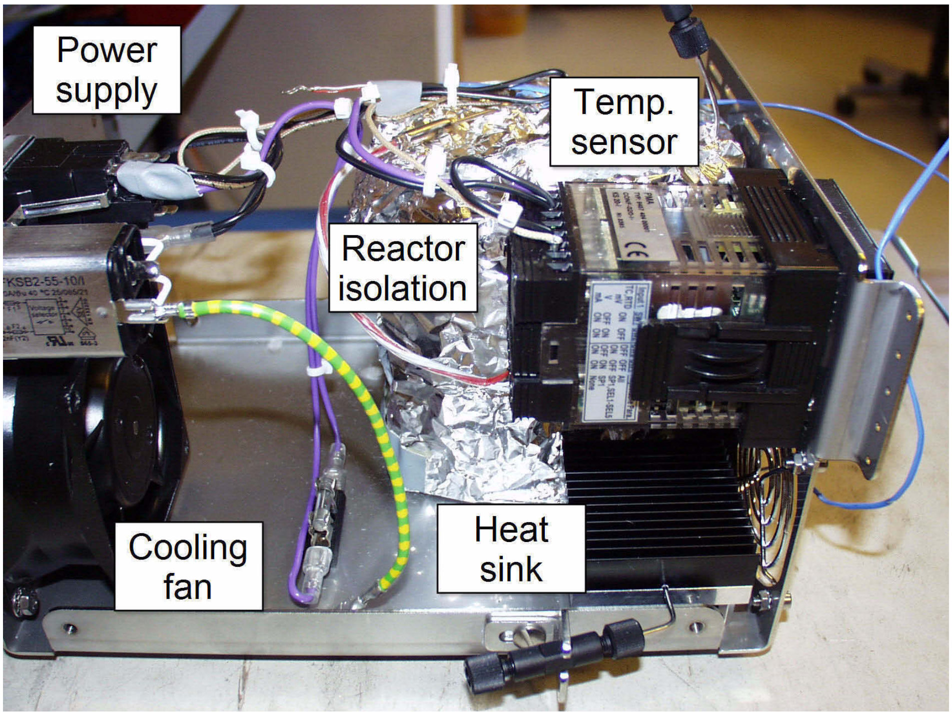


Fig. 3 - 8 Components inside the compact reactor system

3.4.3 Design improvements for the liquid handling system

In addition to the size optimizations, the major modification compared to the basic setup was the use of only one injection valve. To avoid metal parts a 6 port, 3 channel PEEK injection valve (Knauer, Berlin, Germany) driven by a valve motor was used to inject the sample into the high pressure system. Instead of 1/8'' tubings with lower working pressure limits, a 1/16'' tubing was used which was coiled up in-front of the injection valve. For acid and sample handling a PTFE dosing syringe pump (Proliquid, Ueberlingen, Germany) was used to dose sample and acid into the sample loop.

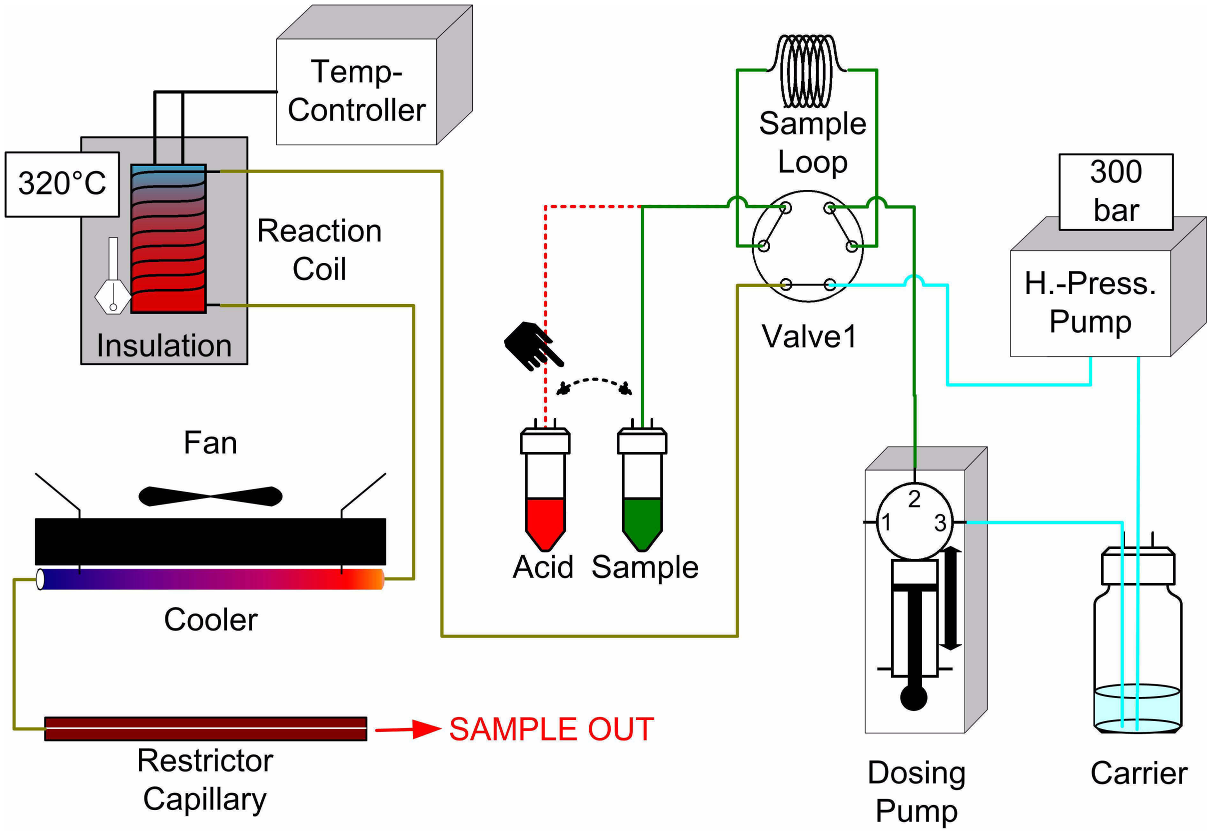


Fig. 3 - 9 Schematic drawing of the modified noble metal digestion system

The dosing pump was controlled by a PC using the RS232 port of the pump. After filling the sample loop with carrier the system was able to take up:

- Acid plug 1
- Sample/acid mixture
- Acid plug 2

by suction into the loop. The changes between the different solutions were done manually by changing the position of the suction hose between the vials filled with sample and acid.

3.4.4 Slurry digestion with a dual reactor setup

The new dual reactor setup was used to run the sample slurries again which had caused difficulties in Berndt's test configuration (see chapter 3.4.1). It was able to show that not even the changes from 1/8" to stronger 1/16" tubings and fittings with higher pressure resistance were enough to cover the extreme increase in pressure. Due to spontaneous reaction of the fast heated sample, the system pressure increased rapidly. The restrictor at the end of the high pressure system did not allow faster release without drastically increasing the system's pressure. These pressure peeks caused almost every time the breakage of the PEEK sample loop, because the better fittings were then able to hold the tubing in the valve. In such a case all the sample, acid and carrier were again vented within seconds. Reducing the flow rate from typically 1.2 mL/min to values below 0.4 mL/min brought lower peaks, but also drastically limited sample throughput.

To overcome the pressure peak issue a second reactor coil with a similar Pt-Ir-capillary (length and diameter) was used. This reaction coil allowed to run a pre-decomposition of the sample material before the very reactive high temperature reactor. Constantly heated to 150℃, the isolated pre-reactor was mounted on the top of the instruments case and inserted between the injection valve and the main reactor. Due to this design it was possible to run the slurries that had previously caused broken or slipped sample loops. It was even possible to apply again higher flow rates, allowing for more samples per hour.

Test settings:
Flow digestion system as described in chapter 3.3.1 with an additional 1.5 m Pt-Ir-reactor at 150℃.

Table 3.9: List of sample slurries applied in the experiments:

Sample	**Weight**	**Reagent** (high pressure system)
BCR 278 Mussel tissue	0.4 g	10 mL 5 M HNO_3
TORT-2 Lobster	0.2 g	10 mL 5 M HNO_3
BCR 62 Olive Leaves	0.2 g	10 mL 5 M HNO_3

Mobile phase:	20 mL HNO_3 / L water
Sample:	2.5 mL (slurry with 5 M HNO_3), nested between 2 x 1.0 mL of 5 M HNO_3
Flow rate:	1.0 mL/min; retention time within the reactor: 80 s
Temperature:	320℃ main reactor, 180℃ for the pre-heating reactor
Pressure:	113 - 176 bar with a restrictor with an i.d. of 64 µm and a length of 49 cm
Collection Volume:	10 mL

Table 3.10: Comparison for a BCR 278 mussel tissue slurry digestion

	Cert. value	**Pt-Ir-System**	**Difference**
BCR 278 mussel tissue	Mean ± SD µg / g	Mean ± SD µg / g	%
As	5.9 ± 0.2	3.70 ± 1.70	-37
Ca	(1000)	1050 ± 40	ok
Cd	0.340 ± 0.02	0.291 ± 0.001	-15
Cr	0.77 ± 0.15	0.74 ± 0.10	ok
Cu	9.6 ± 0.16	6.20 ± 0.01	-40
Fe	133 ± 4	122 ± 9	ok
Mg	(1400)	1320 ± 40	ok
Mn	7.3 ± 0.2	6.90 ± 0.20	ok
Zn	76 ± 2	68.4 ± 1.0	ok
TOC [%]	~ 50 %	3.7 ± 0.1	ok

Table 3.11: Comparison for a TORT-2 lobster hepatopancreas slurry digestion

	Cert. value	**Pt-Ir-System**	**Difference**
TORT-2 lobster hepatopancreas	Mean ± SD µg / g	Mean ± SD µg / g	%
As	21.6 ± 1.8	14.4 ± 3.1	-33
Cd	26.7 ± 0.6	20.0 ± 0.3	-25
Cr	0.80 ± 0.8	0.30 ± 0.01	-62
Cu	106 ± 10	85.6 ± 8.4	-19
Fe	105 ± 13	89.3 ± 8.4	-15
Mn	13.6 ± 1.2	12.4 ± 0.10	ok
Se*	5.63 ± 0.67	7.90 ± 1.50	41
Sr	45.2 ± 1.9	48.2 ± 0.1	ok
V	1.64 ± 0.19	1.60 ± 0.20	ok
Zn	180 ± 6	164 ± 2	-20
TOC [%]	~ 50 %	6.0 ± 0.1	ok

* the Se concentration was close to the detection limit of the used ICP-OES

Table 3.12: Comparison for a BCR 62 olive leaves slurry digestion

	Cert. value	**Pt-Ir-System**	**Difference**
BCR 62 Olive Leaves	Mean ± SD µg/g	Mean ± SD µg/g	%
Ca	-	17600 ± 100	-
Cd	0,10 ± 0,02	0,071 ± 0,010	-30
Cu	46,6 ± 1,8	32,6 ± 0,5	-30
Fe	-	240 ± 24	-
Mg	-	947 ± 14	-
Mn	57,0 ± 2,4	53,2 ± 0,6	-7
Pb	25,0 ± 1,5	21,2 ± 0,5	-16
Zn	16 ± 0,7	11,2 ± 1,5	-30
TOC [%]	~ 50 %	4,6 ± 0,2	ok

Discussion:

The system setup allowed to meet for several elements the certified values within a tolerance of ±10 %. This relative wide range is acceptable for a fast and automated screening system. Depending on the matrix or the concentration range other elements did not gave proper results. Arsenic is one of these elements giving difficulties as the determination with a standard ICP-OES is not the best technique for such low concentrations.

The plant material caused several times a blockade of the narrow restriction capillary. Only a very diluted slurry managed to pass the system without blockade. First trials with 400 and 300 mg within 10 mL reagent caused digestion interruptions. In all cases the reactor or the restrictor were blocked by silicious particles coming from the leaves. The sample amount of 2.5 mL corresponded to a sample weight of 100 mg (BCR 278) or 50 mg respectively. This amount is small or too small to fulfill the minimum dry weight limits. Typically a minimum weight of 100 mg is needed for sample preparation to fulfill the homogeneity requests. This fact explains the relatively high values of the measurements standard deviation.

The application of a pre-reactor for higher concentrated slurries had some disadvantages concerning extended tailing due to longer capillaries and also much higher costs for the additional reaction coil. Another price issue was the corrosion of the tubings at high temperature. For higher chloride concentrations in the sample or by added reagents corrosion remarkably limits the life time of the Pt-Ir capillary at temperature of 300℃ or more.

3.5 Conclusions

The digestion performance of the optimized noble metal high pressure reactor was sufficient for the analysis of some elements in different sample matrices. The modifications of the sample and liquid handling part of the setup offered higher flexibility concerning acid and sample treatment. The use of a pre-reaction coil at lower temperature followed by a high temperature reactor allowed concentrated slurries to be processed. Limitations of the system are the high costs for long capillaries. In addition higher chloride concentrations in the solutions lead to severe corrosion of the capillaries in a relatively short time resulting in too high running costs. Beside the economical limitations, capillaries like the ones tested are no longer available. The producer DEGUSSA was sold and the new owner decided to stop the production of seamless drawn long capillaries.

The new developments shown in the next chapter based on the experiments made with this setup. The design of a lined tubing, used instead of the expensive and no longer available Pt-Ir capillary, is described.

4 Development of high performance lined tubing

The goal of the development was to find the ideal reactor design for longtime high performance operation. Extracting the essence from all flow digestion work in the past, which was described before, would lead to following list of specifications for an ideal reactor:

- chemically inert material
- no or limited metal contaminations
- high temperature stability
- high pressure stability
- compatible with standard flow components
- inexpensive
- available in variable lengths

Reactor tubes made of PTFE-TFM offer high chemical resistance and low contamination values, but are limited concerning mechanical and thermal stability. The Pt/Ir-reaction system offered extreme pressure and temperature stability, acceptable chemical resistance, but at a very high price and limited available lengths.

Regarding the potential and possibilities of the metal capillary system, a novel lined capillary should be developed to fulfill all the requirements mentioned above.

4.1 Basics

The idea to combine PTFE-TFM hoses and metal capillaries failed in the past because many groups had used microwave as heating source and therefore prevented the use of metal tubes. Berndt used a standard lined product offered for HPLC applications, but had difficulties with the connection to valves and collapsing of the tubing [33]. In cooperation with the R&D department of the Anton Paar GmbH a new fitting was designed to overcome the described difficulties by using special PTFE glue and inserting PEEK capillaries as described by Berndt.

The needed key parameters for a successful capillary were found by experiments in the past:

Temperature:	≥ 300℃
Pressure:	≥ 100bar
Volume:	≥ 5 mL
Length:	≥ 2 m

Temperature:

Temperatures of 300℃ are higher than the recommended permanent operation temperature of PTFE, but mechanically well supported PTFE can offer proper operation for several weeks even at that elevated limit.

Pressure:

Using standard PTFE tubings with an o.d. of 1/16", the maximum pressure applicable depends on the wall thickness and the fittings used. To increase the volume of the reactor a thinner tubing with larger i.d. is needed, but it is limited due to the decreasing pressure stability of both, the tubing itself and the fittings. In Table 4.1 typical maximum pressure values are shown for conical fittings[41]. Increased temperatures decrease this values even more. At increased temperature the indicated values are not applicable or only with remarkable constriction of the tubing due to stronger wrenched fittings. The values are valid for conical one-piece fittings 10/32-conical, for example from Upchurch (Oak Harbor).

Table 4.1: Pressure limits for commercial 1/16" fittings and PTFE-tubings at room temperature i.d.

i.d. [mm]	max Pressure [bar]
0.5	144
0.75	72

Volume and Length:

The used 1/16" Pt/Ir-tubing with an i.d. of 1.0 mm and a heated length of 1 m had a reactor volume of:

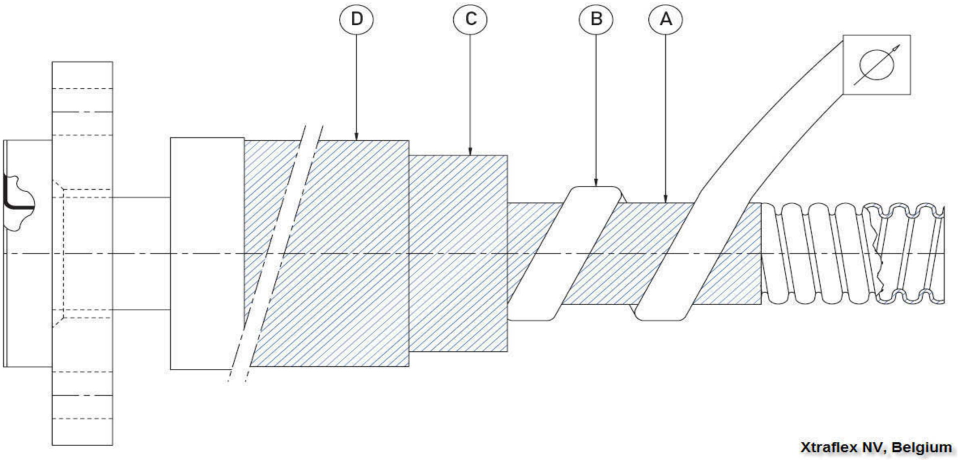
$$V_{1\ \mathrm{m\ Pt\text{-}Ir}} = \frac{\mathrm{i.d.}^2 \cdot \pi}{4} \times l_R = 0.785\ \mathrm{mL}$$

In comparison one meter of a 1/16" PTFE-tubing with an i.d. of 0.75 mm has a volume of 0.44 mL. To reach a reactor volume of 5 mL the reactor needs a length of 11.3 m.

$$l_{5\ \mathrm{mL\ PTFE}} = \frac{5\ \mathrm{mL}}{0.44\ \mathrm{mLm}^{-1}} = 11.3\ \mathrm{m}$$

4.2 Fiber reinforced PTFE tubing

Fluorinated polymer tubings are known for high pressure and temperature applications like mold injection or gas measurement applications. The typical inner diameters lies between 4 and 6 mm up to 25 mm offering pressure and temperature stability of up to 250 bar at 250°C. Heated versions are available to avoid cooling of melted polymer or condensation for combustion gas measurement applications.



Xtraflex NV, Belgium

Heavy wall wire reinforced PTFE liner:

- A. Stainless steel braid for pressure stabilization of the PTFE liner
- B. Self-regulating tracing cable for electrical heating
- C. Insulation layer
- D. Stainless steel (AISI 304) braid for mechanical protection of the tubing

Fig. 4 - 1 Self-heated and fiber reinforced PTFE high pressure tube and fitting

The disadvantage of this tubing are the metal fittings which prevent the use for analytical applications. To overcome this limitations and to apply microwave energy, Haswell and Barclay had to use carbon fibers for tube reinforcement in the heating- and cooling zones and standard polymer fittings at the cold ends of the PTFE pressure hose (see chapter 2.3). The allowed maximum operation temperature and pressure for such a design was drastically lower compared to the steel shielded tubings and the theoretical ideal limits defined above.

4.3 Modified commercial tube with PTFE Liner

For applications with limited need for high flexible tubings the fiber reinforcement can be replaced by ductile metal tubes with an inner layer made of fluoropolymers. Such a commercially available stainless steel tubing was used by Berndt before the experiments with the Pt/Ir-capillary [33]. The liner avoids contact of reagents with the supporting material, but in the end the fittings are located directly on the steel tubing allowing contact with the reagent and causing contaminations.

Berndt therefore inserted short PEEK capillaries in both ends and fixed them with a special fluoropolymer glue to reduce contamination from the supporting metal tube. With such precautions the fitting mainly had contact with the PEEK insert (see Fig. 4 - 2).

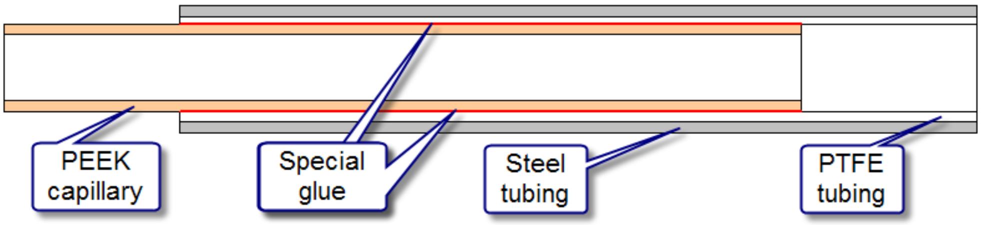


Fig. 4 - 2 PTFE lined tubing with capillary

The inserts also reduced collapsing of the tubing, another effect detected by Berndt. He thought it was a problem of bad mechanical insertion of the liner into the steel tubing. The real cause, diffusion through the liner and thermal expansion, was discovered during experiments for the development of the new capillary and will be described later. The glued PEEK capillary reduced the tendency for collapsing and contamination, but the inner diameter reduction increased the danger of clogging.

4.4 PTFE lined metal tubes

To overcome all determined problems from other lined tubings and to fulfill the needs for high performance flow digestion, a new tubing and fitting design was developed in cooperation with the University of Technology Graz and the R&D department of Anton Paar GmbH in Graz.

4.4.1 Specifications

The following specifications required a new approach to solve the open problems:

1) Fitting to avoid direct contact of media and supporting metal tube

2) Fitting for pressure of more than 100 bar, compatible with standard port connections

3) Producibility of cheap reactors with at least 5 mL reactor volume

4) Electric heating of the tubing

In addition, the requested features for a proper online sample preparation system, defined in chapter 4.1, are still valid.

4.4.2 Stainless steel tube and standard fitting

In feasibility experiments a seamless drawn stainless steel capillary (1.4401) with 1/8'' o.d. and 2.06 mm i.d. formed the supporting shell. The two ends of the capillary were treated to remove sharp edges from the diamond saw cutting process. After that, super flangeless fittings (Upchurch, Oak Harbor) were installed on both ends prior to insertion of the PTFE hose.

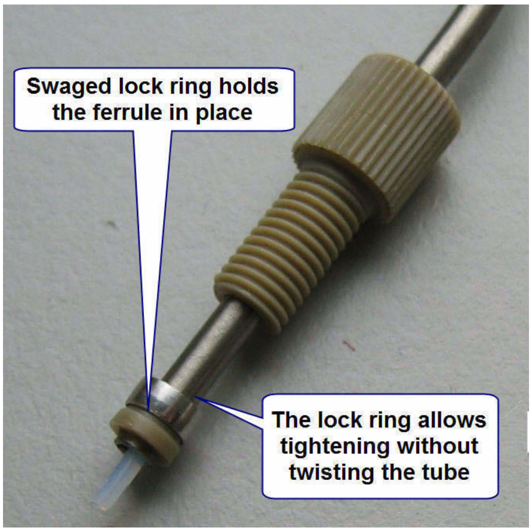


Fig. 4 - 3 Fitting installed on the steel tube with 1/16'' PTFE liner

The difference in o.d. of the PTFE hose and the i.d. of the steel tubing allows inserting the hose into the tube easily, even if it is five meters long. Before the installation of the special fittings the PTFE tubing ends should be 30 cm longer than finally needed.

4.4.3 Fitting and liner

The need for holding the steel tubing and for sealing the PTFE liner guided the way to a solution combining approved fitting designs. As can be seen in Fig. 4 - 4 the conical seal on the front end is identical with standard 1/16’’ 10-32 fittings and can therefore be combined with all standard components like valves or unions. The other end offers an uptake for the 1/8’’ super flangeless fitting of the steel capillary.

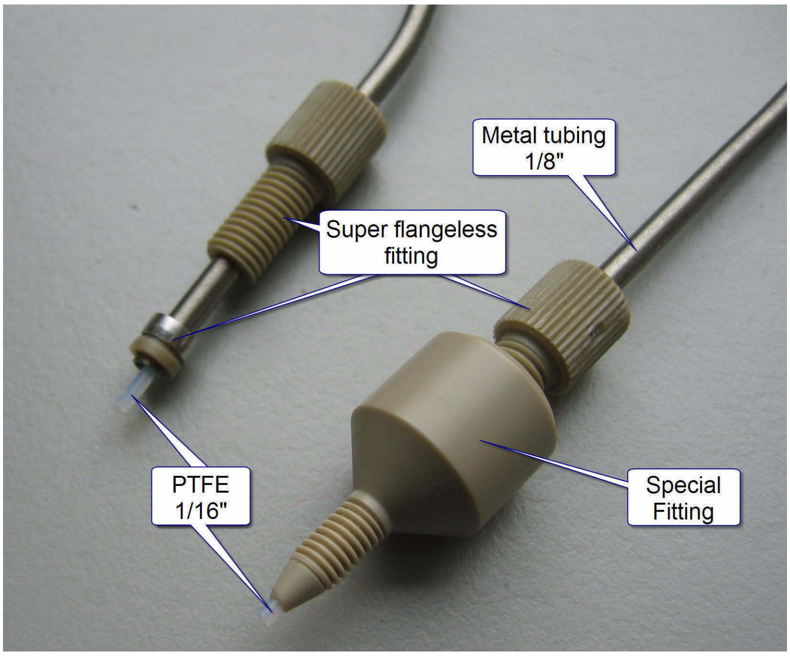


Fig. 4 - 4 Lined metal capillary and new fitting

In comparison to standard one-piece fingerthight fittings, the new fitting needs no extreme tightening because the friction between the supporting metal tube and the PTFE hose avoids typical creeping effects known for simple PTFE tubings in fittings. Loose tightening without remarkable constriction is enough to seal the fitting to a working pressure of 250 bar. On the other hand, the wetted end is only in contact with polymer materials, therefore, contamination from the metal supporting tube is eliminated.

As liner a hose with 1/16’’ o.d. and 0.75 mm i.d., made of PTFE-TFM (a copolymer of PTFE with perfluoropropylene vinyl ether, PPVE) is used. This material offers lower porosity and higher thermal as well as mechanical stability compared to standard PTFE.

When pressure and temperature are applied, the PTFE-TFM tube gets stretches and completely fills out the supporting steel capillary. The final reactor volume can be determined with the help of following calculation:

The PTFE-TFM cross section CS_{PTFE} for 1/16” tubing with 0.75 mm i.d. is:

$$CS_{PTFE} = \frac{\mathrm{o.d.}_1^{\;2} \cdot \pi}{4} - \frac{\mathrm{i.d.}_1^{\;2} \cdot \pi}{4} = 1.57\ \mathrm{mm}^2$$

This material stretches to an o.d. of 2.06 mm during the initial shaping process, therefore the new inner i.d. will be:

$$ID_2 = \sqrt{\frac{\left(\frac{\mathrm{o.d.}_2^{\;2} \cdot \pi}{4} - CS_{PTFE}\right) \cdot 4}{\pi}} = 1.50\ \mathrm{mm}$$

Due to the larger i.d. of the stretched tubing, the reactor volume V_{PTFE} increases compared to the not stretched liner from 0.44 mL per meter (see chapter 4.1) to

$$V_{PTFE_{Streched}} = \frac{\mathrm{i.d.}^2 \cdot \pi}{4} \times 1000\ \mathrm{mm} = 1.77\ \mathrm{mL}$$

$$l_{5\ \mathrm{mL\ PTFE}} = \frac{5\ \mathrm{mL}}{1.77\ \mathrm{mL\ m}^{-1}} = 2.82\ \mathrm{m}$$

Therefore, the reactor and the tubing length $l_{5\ \mathrm{mL\ PTFE}}$ can also be reduced from 11.3 m to 2.82 m to gain the requested minimum volume of 5 mL.

4.5 Flow conditions and heat transfer

In the past beside the coil shape knotted reactors were used to avoid signal widening due to non-ideal plug flow. This shape is not applicable for the metal tubing, therefore it is important to avoid turbulent flow by choosing correct mechanical dimensions. Based on the values seen above the flow conditions and heat transfer rates have been calculated.

4.5.1 Determination of the Reynolds number

This length reduction will help to reduce the sample plug broadening due to non ideal flow through the reactor.

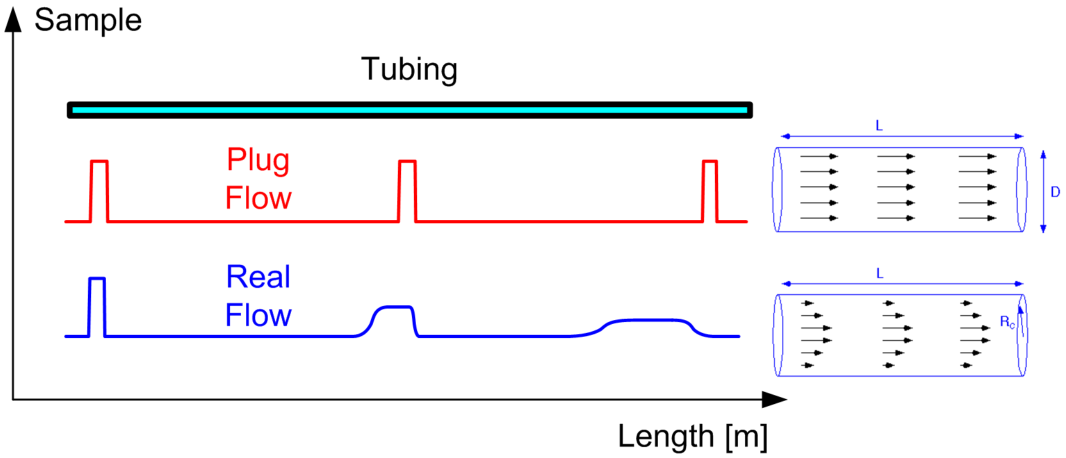


Fig. 4 - 5 Ideal and real flow through a tube

The Reynolds-number can be used to check if the flow inside a tube is laminar or turbulent. Laminar flow is a prerequisite to guarantee plug flow. Reynolds-numbers below 2300 indicate stable laminar flows, above 2300, however, the flow may become turbulent. The calculation for an expanded PTFE-TFM tube and a maximum flow rate fr_{H2O} of 5 mL/min lead to a Reynolds-number RE of:

$$Re = \frac{v_{H_2O}\cdot \mathrm{ID}_2}{\upsilon_{H_2O}} = \frac{\frac{fr_{H_2O}}{A_{H_2O}}\cdot \mathrm{ID}_2}{\upsilon_{H_2O}} = \frac{\frac{fr_{H_2O}}{\frac{\mathrm{ID}_2^2\cdot\pi}{4}}\cdot \mathrm{ID}_2}{\upsilon_{H_2O}} = 70.7$$

v_{H2O} = flow speed; fr_{H2O} = flow rate ; υ_{H2O} = kinematic viscosity of water (= 10^{-2} cm² s^{-1})

The Reynolds number indicates stable laminar flow in the reactor, even if the diameter or flow rate increase remarkably.

4.6 Heat transfer calculations

With the help of a relatively simple part it was possible to fulfill the first three points in the specification list, after that only the question for proper heating was left open.

The thermal properties of the Pt/Ir-capillary were excellent concerning heating and cooling rates. On the contrary, a medium temperature pre-reactor for reactive samples was necessary to slow down heating rates. For the new setup with a PTFE-TFM liner in a metal tube longer heating and cooling times were expected. With thermodynamic calculations the difference should be investigated and the reactor lengths and retention times optimized to gain comparable results to the Pt/Ir-capillary.

4.6.1 Heat transfer calculations for metal and lined metal capillaries

Heat transfer calculations, based on mechanical and physical data from the Pt/Ir and the metal/PTFE-TFM tubings, were done. The goal was to find appropriate lengths for the reactor and the cooler to get comparable results for both techniques. The detailed calculations with all thermodynamical parameters have been done using a MathCAD model of the reaction tubing at the R&D department at Anton Paar.

Following calculation model parameters and values have been defined for the calculations:

Parameters for Pt/Ir and steel/PTFE-TFM:

Table 4.2: Mechanical and physical properties of reactor tubes

Parameter	Pt/Ir tube	Steel/PTFE-TFM
o.d. 1 [mm]	1.8	3.2
i.d. 1 [mm]	1.0	2.2
o.d. 2 [mm] PTFE-TFM	-	2.15
i.d. 2 [mm] PTFE-TFM	-	0.6 ; 1.1 ; 1.5
Air gap [mm]	-	0.05
Flow rate [mL/min]	2 / 4	2 / 4
T_{in} [K]	297.15	297.15
T_{goal} [K]	617.15	547,15 ; 597.15

- metal tubing wrapped around a heating block at constant temperature
- thermal conductance paste between the metal tubing and the heating block
- reaction tube fixed via aluminium-sleeves on the heating block with groovings and insulated

Details for steel/PTFE-TFM:

- The inner liner expands to the steel tube's inner wall due to pressure and temperature.
- Between the PTFE-TFM and the steel tube an air gab of 0.05 mm is postulated; in real tubes a gapless contact is more likely as PTFE-TFM would be shaped smoothly onto the walls.

Following variables were changed to investigate their influence:

- flow rate through the reactor
- i.d. of the PTFE-TFM liner

Heating time results for the steel/PTFE-TFM capillary:

Table 4.3: Heating time and tubing lengths for lined steel tubings

Flow rate	**final temperature 300℃**	**i.d. = 0.6 mm**	**i.d. = 1.1 mm**	**i.d. = 1.5 mm**
4 mL/min	Heating time (s)	26 s	76 s	144 s
	Heating length (m)	6.13 m	5.53 m	5.43 m
2 mL/min	Heating time (s)	n.c.	78 s	93 s
	Heating length (m)	n.c.	2.76 m	1.83 m

n.c...not calculated

Heating time results for the Pt/Ir capillary:

Pt/Ir-capillary:2 mL/min; heating block at 320℃; 1500 mm tubing length (without pre-heating coil)

heating time to 300℃:	14 s
length of the heating zone:	600 mm

As can be seen in Table 4.3 the media in the combined PTFE-TFM/metal capillary with i.d. 1.5 mm liner thickness would need more than two minutes to reach the set temperature. This fact would help to avoid spontaneous reactions as have been seen for the fast heating Pt/Ir-capillary. The main reason is the 65 times higher thermal resistant coming from the PTFE-TFM-liner. To adapt the heating time the liner thickness needs to be adjusted. A configuration with a liner having only 0.2 mm wall thickness needs double the time compared to the metal capillary of Berndt. To simulate the used low temperature pre-reactor (chapter 3.4.4) with moderate heating rates a wall thickness of 0.35 mm for the shaped PTFE-TFM liner was chosen. This configuration would heat the media to working temperature of 300℃ within a little bit more than 1 min avoiding spontaneous reactions.

4.7 Directly Heated Reactor

To avoid additional mechanical parts a direct heating technique was tested first. A 150 cm steel capillary with PEEK fittings, as described in chapter 4.4.2, was used. For heating purposes only a transformer, used to apply low voltage and high amperage to the steel tubing, was necessary. Two copper clamps were installed to connect the tube with the transformer.

4.7.1 Configuration

In Fig. 4 - 6 the scheme of the setup can be seen. Two peristaltic pumps were used to load the sample loop at the injection valve with acid and sample. A programmable controller was used to set temperature, adjust sample and acid amounts and control the injection valve. Instead of the capillary a pressure regulation valve made of PEEK with a fluoro-plastic membrane was used. The advantages of the valve are the easy adjustment to the needed working pressure as well as the fact that the pressure increases only little when changing the flow rate. Generally, the valve has a pressure fluctuation of only 10% at flow rates between 0.1-10 mL/min. Another positive effect is the larger bore hole in the valve (approximately 0.3 mm) instead of < 0.1 mm for the capillaries used before.

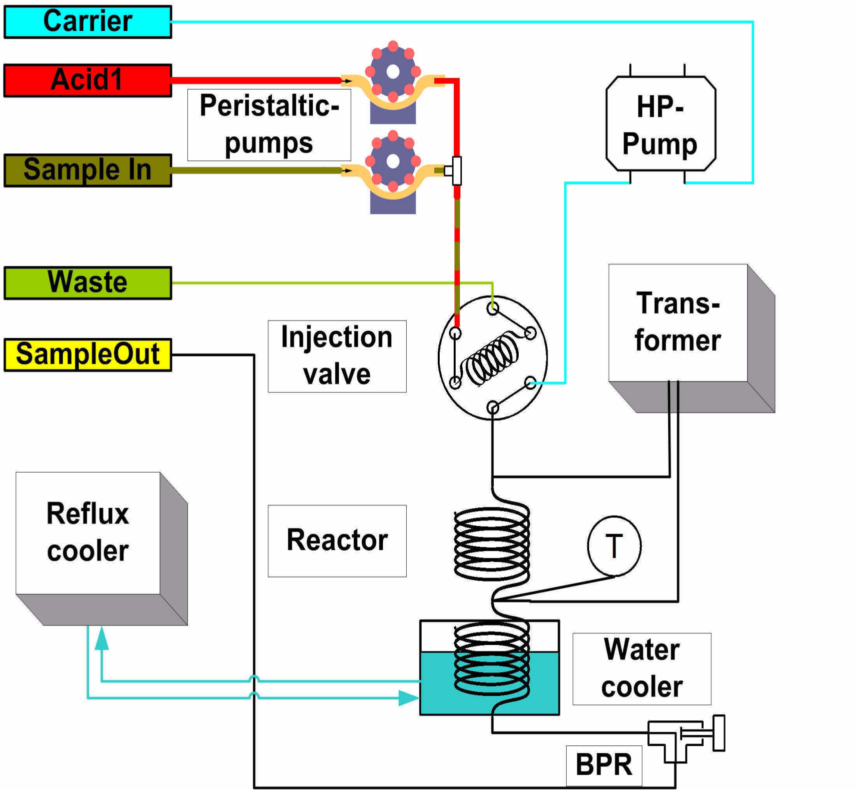


Fig. 4 - 6 Flow chart for the directly heated reactor setup

4.7.2 Power Supply

As the tubing has a relatively low electric resistant, high current was necessary to reach the needed heating rate. To gain 100 W heating power the needed amperage can be calculated as follows:

Electrical resistant of the steel tubing:

$$R_{Steel} = \frac{\rho \times l}{A_{\mathrm{o.d.}} - A_{\mathrm{i.d.}}} = \frac{444 \times 10^{-6}\,\Omega cm \times 150 cm}{4,24 \times 10^{-2} cm^2} = 1,57\ \Omega$$

R_{Steel}...resistant of the tubing ; ρ...specific resistance ; l...length ; A_x...cross section

Needed power supply for 100 W heating:

$$P = \frac{I^2}{R_{\mathrm{Steel}}} \qquad I = \sqrt{\frac{P}{R}} = \sqrt{\frac{100}{1,57}} = 7,98\ A$$

P...Power ; I...electric current ; R_{Steel}...resistant of the tubing

Setup:

A microwave magnetron heating transformer (Whirlpool, Surrey, UK) was used in combination with an adjustable transformer (Elin, Weiz, Austria) to deliver the needed amperage and adjust the power. Typically, the primary voltage of the heating transformer was adjusted between 150 V and 175 V to reach and hold temperatures of 260 to 320°C. One electric contact clamp was installed 100 mm after the entrance to protect the inlet fitting against high temperatures, the other one right above the water cooler coil. To control the temperature of the system a thermocouple sensor was used. For installation of the sensor, heat-conductive paste was used for good thermal contact. The thermocouple was isolated with teflon to resist the high operation temperatures. Before the operation, the setup was isolated by using several layers of approximately 1 cm thick fine glass wool (Merck, Darmstadt, Germany) fixed on an aluminium film. The temperature was regulated manually by the voltage of the transformer to maintain a constant temperature at a chosen flow rate. Fig. 4 - 7 shows the setup with indicated electric clamps and the temperature sensor, but without the glass wool insulation.

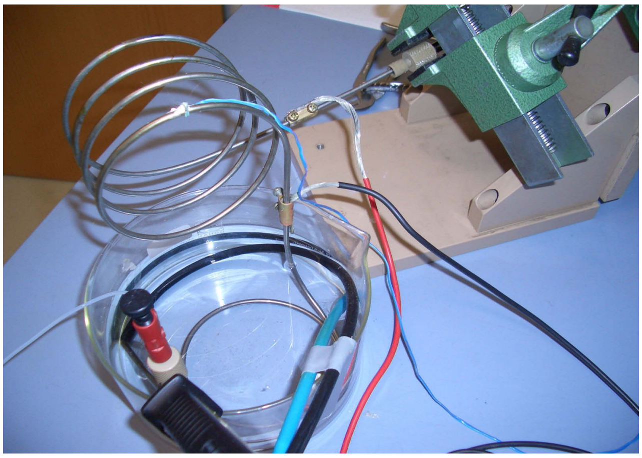


Fig. 4 - 7 Direct heated reaction coil with sensors and backpressure regulator

4.7.3 Experiments

The system described above was used to run performance and stability tests, in which a diluted nitric acid solution (1:10 diluted concentrated nitric acid 65 %) was used. The pressure settings should be around 150 bar, the temperature should be 275°C at a flow rate of 2 mL/min.

Before heating, the system was set under pressure by closing the adjusting screw of the pressure regulator, after the HPLC pump had been activated. It was important to increase pressure only slowly after having reached the 80bar margin of the used PTFE-TFM tubing with 1.6 mm o.d. and 0.75 mm i.d. The PTFE-TFM hose needed some pumped volume and time to get shaped to the supporting tube. The time needed for the shaping process can be calculated by the gap volume between the used PTFE-TFM tube, the inner diameter of the steel capillary and the flow rate.

$$t_{shape} = \frac{V_{gap}}{v_{flow}} = \frac{(A_{tube} - A_{PTFE}) \times l_{tube}}{v_{flow}} = \frac{(0,0381\,\mathrm{cm}^2 - 0,0201\,\mathrm{cm}^2) \times 150\,\mathrm{cm}}{2\,\mathrm{mL/min}} = 81\,\mathrm{s}$$

The first reactors withstood the adjusted parameters only for a short period of time, namely one to maximally two days. Pressure increased slowly, which led to a complete blockade at the end of the first or second day. In such a case, the HPLC-pump stopped by reaching the alarm pressure level. The pressure stood high even the adjusting backpressure valve was completely opened.

Analysis of reactor failure

It was impossible to pull out the PTFE-TFM hose from the tubing to investigate the reason for the blockade. Therefore, the steel tubing was cut carefully with the help of a diamond disk saw. The released PTFE-TFM hose completely collapsed at the end of the heated zone, whereas the part at the beginning and inside the cooling zone was still in shape.

A microscope was used to take pictures of the damaged tubing. The first picture shows the tubing in the middle of the reactor, the second one close to the end of the heating zone and the completely collapsed part while the last one shows the hottest area near the conducting clamp. In this last picture the tubing also shows milky white spots within the opaque standard material. These spots are known from batch microwave systems and indicate too high reaction temperatures. It seems that the temperature sensor was installed too far away from the conduction clamp, which allowed that higher temperatures reach the end of the zone. Another reason for over-temperature could be the stopped flow after the pump stopped leading to higher temperatures at constant voltage. The black particles on the tubings are the result of the cutting process.

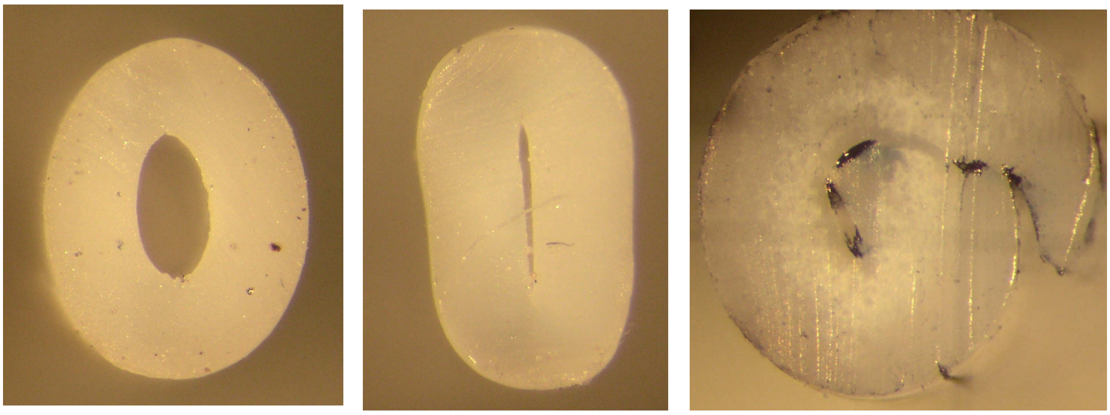


Fig. 4 - 8 Microscope pictures of the collapsed PTFE-TFM reaction coil

Berndt also detected collapsing tubings during his experiments and thought it was a mechanical problem of the tubing. He was able to run for two or three weeks due to lower temperatures, but finally also had a damaged hose.

The real explanation could be found during further experiments and modifications: reagents diffused through the PTFE-TFM material and were trapped between liner and steel tube. After a while, the pressure outside the liner was similar to the pressure inside, which caused collapsing of the PTFE-TFM tubing. Due to the very large thermal extension factor of PTFE-TFM the perimeter of the polymer tubing expanded much more than the inner perimeter of the steel tubing. As long as the inner pressure was higher than the external pressure, the hose was pressed to shape. Due to diffusion through the PTFE-

TFM hose the pressure in the gap between the PTFE-TFM liner and the steel tubing increased slowly. At equilibrium the stabilizing force got lost and the expanded larger hose collapsed as can be seen in chapter Fig. 4 - 8.

Thermal expansion coefficient: PTFE-TFM:115 10^{-6}/K
Steel: 17,3 10^{-6}/K

Thermal expansion:

Inner diameter of the tubing: 2.2 mm

Temperature difference: 280 K (from room temperature to 300℃)

PTFE-TFM: $\Delta Perimeter_{PTFE} = 115 \cdot 10^{-6} \cdot \Delta T \cdot d \cdot \pi = 0.22\ \mathrm{mm}$

Stainless Steel: $\Delta Perimeter_{Steel} = 17.3 \cdot 10^{-6} \cdot \Delta T \cdot d \cdot \pi = 0.03\ \mathrm{mm}$

This relatively small extension is enough to lead to the collapse of the tubing as shown in Fig. 4 - 9. This effect can take place slowly over hours or days or within seconds, if the pressure inside the hose drops fast. This happens when the pump stops or after a quick release of pressure with the help of the back pressure regulator at high reactor temperature. In such a case, the pressure of the liquid between the PTFE-TFM hose and the steel tubing will push the tubing to the center.

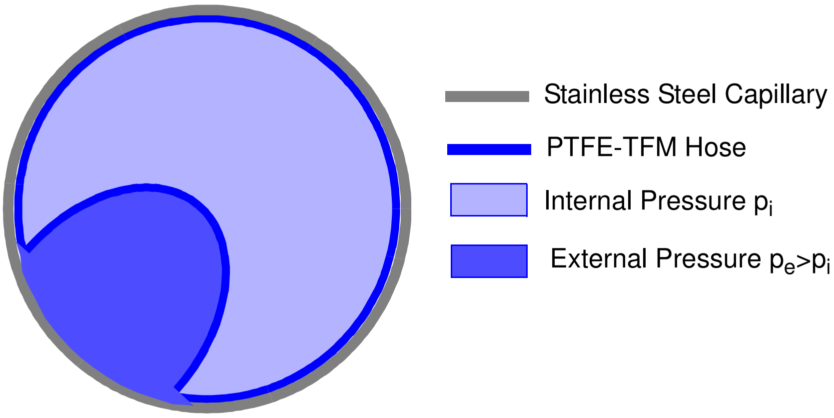


Fig. 4 - 9 Collapsed PTFE-TFM hose inside the stainless steel tube

4.7.4 Drain port in the fitting

To avoid the negative effects of the diffused material, a drain port in the fitting was investigated to allow the release of the diffused liquid before the liner will be damaged. The new fitting therefore got an additional hole with an inserted tube to a collection container (see Fig. 4 - 10).

Fig. 4 - 10 Fitting with drain port and collection vial

After installation of the drain port it was possible to run the reactor for weeks before the liner got damaged. Approximately 0.5 to 1.0 mL / day diffused carrier could be collected with a new reactor. This relatively small amount nevertheless was enough to damage systems without drain port. At the end of the lifetime diffusion increases within few days up to 25 mL / day (Fig. 4 - 11). This allows to indicate the condition of the tubing by measuring the diffused liquid daily. From an analytical point of view even the increased volume of drainage could be ignored compared to 3.0 or 4.0 L carrier per day through the reactor.

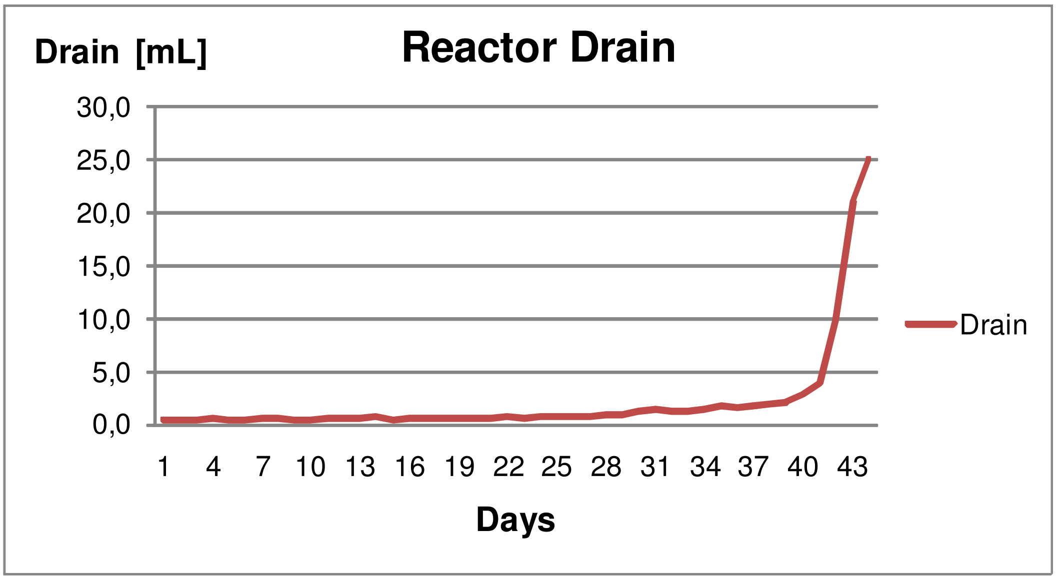


Fig. 4 - 11 Collected drain volume per day for a new reactor tubing

4.7.5 Thermal distribution

After solving the diffusion problem, the thermal inhomogenity of the directly heated reactor was the next issue to optimize. A second temperature probe was installed 50 cm after the injection position to check temperature distribution of the coil. This sensor was mounted by means of a copper film and heat-conductive paste. The complete coil was isolated with glass wool.

During the heating phase the second temperature probe at the beginning of the reactor indicated a very low temperature compared to the sensor at the end of the reactor. This indicated that even the good thermal conductivity of the metal tube was not sufficient to equalize the temperature along the tubing against the stream of the medium inside the reactor. Therefore, an additional electric contact was applied near the central sensor allowing two different electric supply levels. There was one heat up zone at the first quarter of the reaction coil and a hold zone for the rest. Nevertheless the problem could still not be solved completely. The internal flow caused still a complete temperature gradient. By means of an IR camera it was possible to show that the reaction coil now heated faster from room temperature to an elevated temperature at the central connection point. The temperature then increased further to the maximum temperature at the end of the heating zone to 300℃. There was no zone at constant high temperature needed for good digestion results. In addition to the bad digestion performance the setup used two power supplies, two sensors and controllers. This foiled the idea of having a simple setup. For that reasons the next experiment was made with a digestion coil allowing equal heating and simple control.

4.8 Heating the reactor with a heating block

To overcome the inhomogeneous heating problem observed with direct heating, a heating coil on a heating block was designed. The lined reaction tube was wrapped around an aluminium husk with a thread. This design offers better contact than Berndt's described cylinder and clamp solution. Now it was possible to cover the tube form 180° instead of having only two contact points. Furthermore, this husk on a large heating block gives enough thermal capacity to keep the system at constant temperature even at changing flow rates.

4.8.1 Design

The design with a thread, slightly smaller than the tube, should guarantee perfect heat transfer by reducing the air gap between the coil and the tube. During production the tube will be pressed into the coil for good thermal contact. In Fig. 4 - 12 the reaction tube, perfectly fitted in the coil, can be seen. The aluminum coil and the heating block are hard-anodized to protect the surface against oxidation. Without that measure the coil would permanently stick to the heating block after several weeks of operation. Additionally a high performance Molybdenum heat-conductive paste (Molykote P37, Dow Corning, Midland, USA) was used to avoid permanent adhesion between the coil and the heating block.

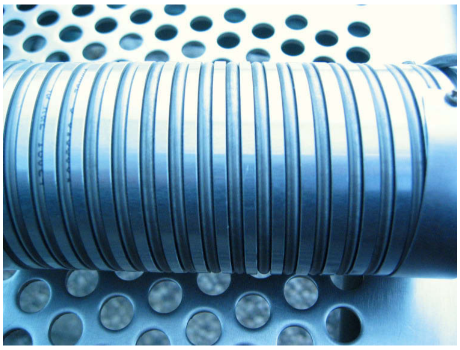


Fig. 4 - 12 Wrapped reactor tubing in an aluminum coil

4.8.2 Thermal homogeneity

In Fig. 4 - 13 the same reaction coil is shown by using an IR camera which indicates the excellent thermal homogeneity. According to the needs of the application it is possible to expand or shorten the central heating block for a third of its length (see Fig. 4 - 13). This design allows to run a kind of pre-heating at slower heating rates due to a cooler part of the coil for critical samples. Further experiments have shown that this feature was not necessary due to the isolating effect of the PTFE-TFM liner. Samples get heated slower which avoids the seen spontaneous reactions. Beside a short block could not influence the temperature of the coil drastically. In Fig. 4 - 13 a short block was used, but the coil has almost the same temperature all over the length.

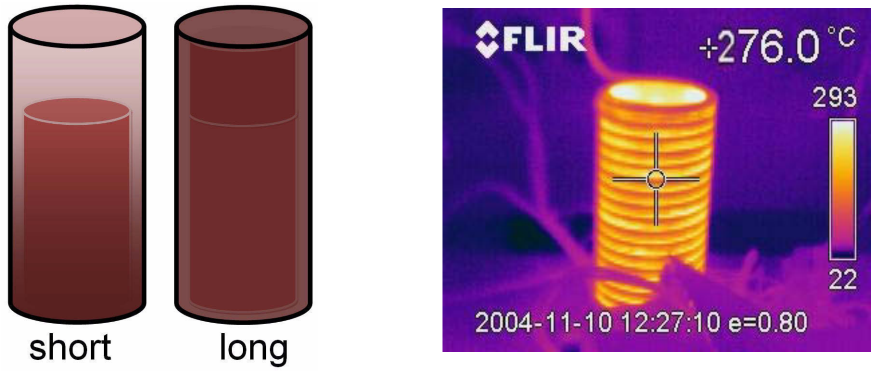


Fig. 4 - 13 IR scan of the reactor with a short heating block showing homogeneous thermal distribution

4.9 Performance verification of lined tubings

4.9.1 Composition of tested tubing materials

In addition to decomposition quality, the other important issue for analytical applications is the blank level of the system. As high blank values would limit the field of applications the influence of the supporting tubing was tested. Because of diffusion trace elements may be transported from the supporting tube to the carrier stream.

Two different materials were tested to see the influence of the tubing material. First reactors made of stainless steel (material code 1.4401) were investigated, afterwards a reactor made of titanium Grade 4 (material code 3.7065). Titanium was chosen as it offers excellent chemical resistance against nitric and hydrochloric acid, a mixture the steel tube won't resist for a long time. Another advantage of titanium is the very low trace metal content. Table 4.4 shows the composition of stainless steel 1.4401 compared to the element concentration in titanium Grade 4 (Table 4.5). Apart from Fe and non-metals the content of other metals in titanium is very low and reduce the danger of contamination.

Table 4.4: *Element composition of Stainless Steel 1.4401*

Element	**Stainless Steel 1.4401** [%]
Non-metals	
P	0.045
S	< 0.03
C	< 0.07
N	<0.11
Si	< 1.0
Metals	
Cr	16.5 - 18.5
Ni	10 - 13
Mo	2 - 2.5
Mn	< 2.0

Table 4.5: *Element composition of titanium Grade 4 (3.7065)*

Element	**Titanium Gr. 4 3.7065** [%]
Non-metals	
O	0.35
H	0.015
C	0.08
N	0.05
Metals	
Fe	0.30
others	< 0.4

4.9.2 Thermal stability comparison for different tubing materials

Parallel to different metal tubings alternative fluoroplastic hoses made of PTFE-TFM, PFA or standard PTFE were tested as liners. The interest for this comparison were different properties due to the production techniques used for PTFE and PTFE-TFM and PFA tubings. PFA tubings are made via extrusion from melted granulate, PTFE and PTFE-TFM hoses need to be sintered. A paste made of tiny PTFE particles is extruded and the raw (green) hose will be transported through a hot tube oven to get sintered to the final product. On one hand PTFE-TFM, and even more PTFE have higher porosity compared to the melted PFA material, but on the other hand also better thermal stability. Lower porosity of the PFA material should help to decrease diffusion, whereas higher thermal resistance will allow higher temperature gaining in better decomposition rates.

For the experiments the test reactors temperature was set between 260℃ and 320℃ and the pressure within a range of 140 to 180 bar.

Support-tubing 1/8” x 2.2 mm with PTFE-TFM or PFA liner; both 1/16” x 0.75 mm

The reactors were heated first using the direct electrical heating setup with a heating time of approximately 15 min from room temperature to maximum 320℃. The power and temperature control for direct heating was regulated manually during the heat-up and constant heat phase. For the second test series a heating block setup with a temperature controller was used.

Table 4.6: Reaction tubing tests with direct heating (via transformer)

#	Liner	Temp. [°C]	Press. [bar]	Serv. time [hours]	Notes
1	PTFE	260	150	23	Std-PTFE material; liner tubing leakage
2	PTFE	260	150	13	Std-PTFE material; liner tubing leakage
3	PTFE-TFM	260	140-195	168	PTFE-TFM material; test stopped after diffusion rate >1 mL/day
4	PTFE-TFM	260	150	96	PTFE-TFM material; test stopped after diffusion rate >1 mL/day
5	PFA	260	150	91	PFA material; test stopped after diffusion rate >1 mL/day

Table 4.7: Reaction tubing tests with a heating block

#	Liner	Temp. [°C]	Press. [bar]	Serv. time [hours]	Notes
6	PTFE-TFM	320	160	16	thermal destruction of the liner; corrosion of tubing
7	PTFE-TFM	320	150	4	thermal destruction of the liner; corrosion of tubing
8	PFA	280	160	17,5	high temperature tests PFA liner tubing leakage
9	PFA	300	160	0	breakage at 293°C; melted liner

Conclusion:

Due to the lower thermal stability and service time of PFA pre-tested PTFE-TFM-tubings were applied for all further experiments in the project. The pre-test consisted of a pressure stability tests with water at 40-50 bar for 1 min. Additionally the cleaning procedures of the titanium tubings as well as the startup-procedure were optimized to increase service time and reliability of the reactors. For details see chapter 4.10.

4.9.3 Analytical determination of blank values

The contaminations from the titanium tubing Grade 4 (3.7065) were determined at the University of Technology Graz at the institute for Analytical Chemistry using a Perkin Elmer Elan 6000 ICP-MS.

Titanium-Capillary:
Following elements were determined:
As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, V and Zn
For some elements, the limits were below the determination limit of 100pg/L, namely for:
As, Be, Cd, Co, Cu, Li, Mg, Mo, Pb, Sb, Se, Sr

For the other elements, following concentrations were determined in the collected samples:

Sample	Ca [µg/L]	Cr [µg/L]	Fe [µg/L]	Mn [µg/L]	Ni [µg/L]	Ti [µg/L]	Zn [µg/L]
Blank	78.0	7.6	22.1	6.7	10.1	7.6	10.0
PFA 260℃ (first startup)	161	426	861	56.0	362	182	34.6
PFA 280℃ (18h operation)	84.5	352	110	11.1	44.9	156	37.3
PTFE-TFM 280℃ (first startup)	185	500	943	61.2	400	260	22.7

4.9.4 Digestion of pure organic test materials

After seeing the practical benefits of the lined tubing design, digestion results were compared to results gained through other flow techniques, such as the AutoFlow operated at 240℃ as well as a comparison to the performance of Berndt's Pt-Ir-reactor. The lined reactor had a lower digestion performance due to lower temperatures compared to the Pt/Ir system with pre-reaction coil, but succeeded in comparison with the AutoFlow indicating the importance of highest possible digestion temperatures.

Table 4.8: TOC measurement after flow digestion using pure organic test materials

(n = 5)	**TOC [%]**	**TOC [%]**	**TOC [%]**
Sample Solutions 1%	**Pt/Ir dual coil 80 s @ 180/320℃**	**PTFE-lined reactor 240 s @ 300℃**	**AutoFlow reactor 240 s @ 300℃**
Glucose	2.4 ± 0.4	4.3	6
Glycine	1.4 ± 0.1	10.1	38
Phenylalanine	26.9 ± 1.7	-	-
Nicotinic acid	47.6 ± 3.2	~ 100	-

4.10 Reactor optimization

After starting with standard steel tubings and standard PTFE-TFM hoses, many different optimization steps were obtained during the development to increase service times and production process reliability. In this chapter, the different optimization steps are collected, which take in sum almost 3 years because long time stability tests between the different steps were necessary.

The development, major improvements and experiments have already been described in the sections before, therefore, the following chapter will describe only minor, but still important improvements from following starting point:

- Supporting metal tube: titanium Grade 4; 1/8" o.d., 2.2 mm i.d.
- Liner: PTFE-TFM 1/16" o.d., 0.75 mm i.d.; (pressure test before insertion: 50 bar / 1 min)
- Fitting: one fitting for 1/16" tubing with drain port

4.10.1 Process improvements

During first investigations some extracted liners showed damages or traces of black particles, which were attributed to the inner side of the titanium tubing. To prevent further damages from remaining particles of the tube drawing process, additional cleaning with brushes was used before rinsing with isopropyl alcohol. These small tube brushes are made of polyamid fibers coated with SiC, or in our case, industrial diamonds, as grinding material (TIP, Klosterneuburg, Austria). Fig. 4 - 14 shows such micro-abrasive brushes available for different tubing diameters. To pull the brush through the tubing, a 4 m steel wire was laser-welded on the short brush.

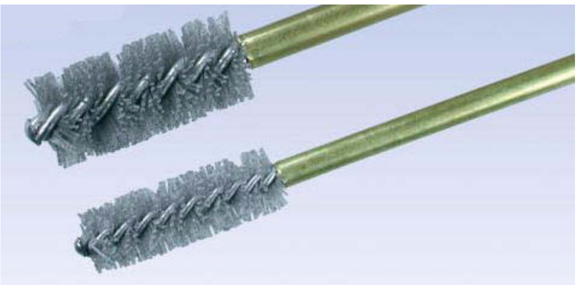


Fig. 4 - 14 Micro-abrasive nylon-diamond tube-brushes

Another point that had to be improved was the first shaping process of the PTFE-TFM liner. During the first trials the reaction tubings were pumped up to the final pressure before heating the reactor. At a pressure of approximately 100 bar, the pressure increase stopped because the hose started to expand inside the supporting hose. After filling the gap between the non-shaped liner and the inner diameter of the hose, the pressure further increased until it reached the adjusted pressure of the system. The disadvantage of that procedure was that the shaping of a cold and therefore stiff tubing could give inhomogeneous wall thickness over the length. In cooperation with the manufacturer of the liner material (Elring-Klinger, Dettingen, Germany) a procedure at elevated temperature was developed, running the first shaping process at following conditions:

1) pressure build up to 40bar at room temperature

2) stopping the pump and start heating up to 220℃

3) restart the high pressure pump at low rate to shape the soft tube until reaching minimum 100bar

4) continue heating until reaching the starting temperature, normally 300℃

Step 1) will guarantee that the pump is ready to use and not filled with air, step 2) will allow fast heating to the tube shaping temperature and making the hose soft for easy and homogeneous shaping.
During step 3) the tubing will get shaped; the heated part in the reaction coil area will be shaped at approximately 80-85bar (indicated by stable pressure at constant pump rate). After complete shaping in the heated zone, the pressure increases until the tubing inside the cooler areas is shaped. At the end of the shaping process the pressure will increase fast until it reaches the set pressure. The shaping process at high temperature will give more reliable and homogeneous wall thickness increasing the service time. Finally Step 4) will bring the system to the starting temperature. In this phase of the process, the pump runs at low intensity. A stopped pump could lead to collapsed tubings if the reagents inside the tubing are released by the back pressure valve whereas pump rates at normal process speed would extend the heat up-time of the system.

4.10.2 Extension fittings

In case of a blocked reactor tubing it is necessary to remove the special fitting at the and to reinstall it after cleaning. The conical part of the fitting gets deformed during use. That is why the fitting will push the short liner, pointing out of the titanium tubing, back into it. This means the reactor can not be serviced without special measures as the fitting cannot be re-applied. To avoid the total loss of the reactor in such a case extension fittings were introduced. After removing the sealing fitting and rinsing the liner one of the several extension fittings, mounted between the reactor tubing and the fitting, could be removed extending the length of the free liner (Fig. 4 - 15).

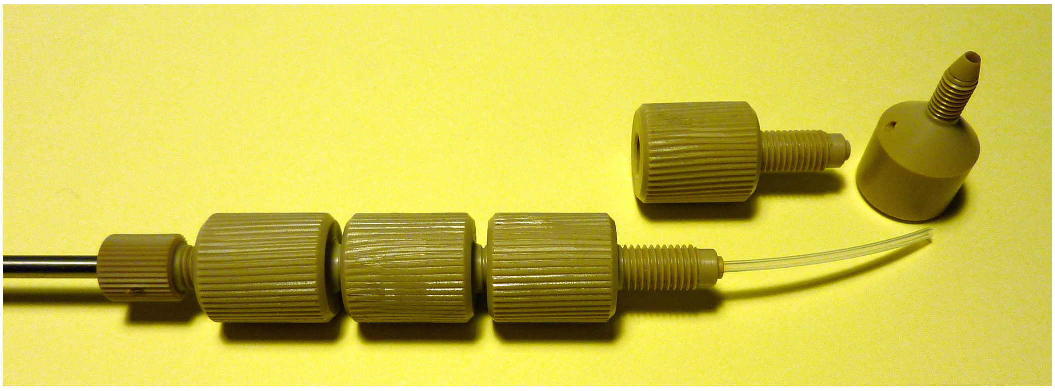


Fig. 4 - 15 Lined reactor with removed sealing- (right) and extension- fitting (left)

Now it is possible to fix the longer PTFE-TFM tubing while mounting the fitting again (see Fig. 4 - 16), otherwise the conical part would push the liner only into the tubing.

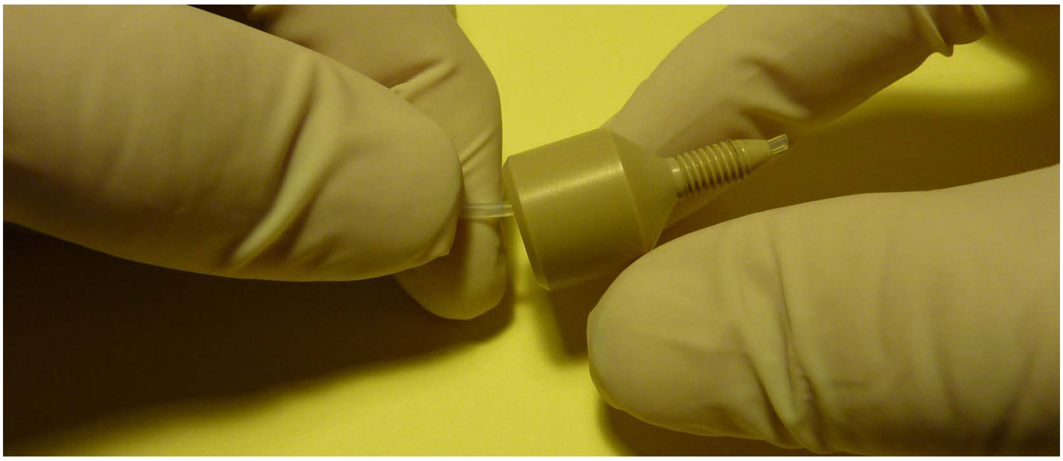


Fig. 4 - 16 Reinstallation of the fitting while fixing the liner

After screwing the fitting to the stop the extended liner needs to be cut (Fig. 4 - 17) and the reactor is ready to be reinstalled in the system. Depending on the number of extension fittings it is possible to clean and maintain the reactor tubing several times before replacement.

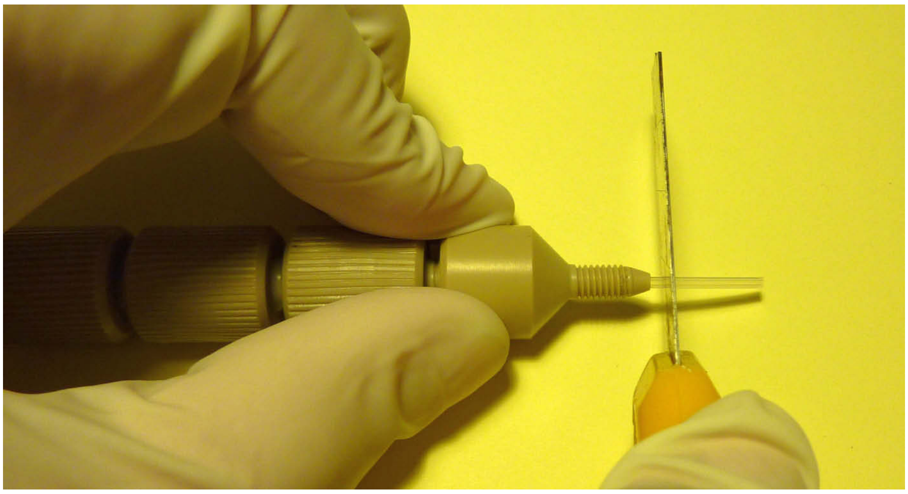


Fig. 4 - 17 Adjusting the length of the tubing

4.10.3 Low expansion tubings

The most important improvement for the service time was the increase of the PTFE-TFM liner tubing diameter. Special tubings which had an o.d. that was only 0.1 mm smaller than the i.d. of the supporting tubings are made to prepare reactors with extremely low expansion rates. For the new tubings it is necessary to insert them with the help of a wire to pull the liner through the brushed and rinsed tubing. With the smaller original liner it was possible to insert the hose only by pushing it through the titanium tubing. This simpler technique is still possible for shorter lined tubings using the new PTFE-TFM hose up to maximally 2 m, but above that length it is necessary to pull the liner.

To keep the reaction condition constant it was necessary to adapt the liner wall thickness for the new tubing in order to have a similar PTFE-TFM layer between the heated tubing and the sample. A thinner liner would result in reduced heating and cooling times, but at the cost of higher diffusion rates and possible spontaneous reactions. Thicker liners would limit the risk of spontaneous reactions and diffusion, but it would also increase the heating and cooling times. This would lead to bad digestion results as the samples remain shorter at high temperature when using the same reactor size.

To order a tube with similar wall thickness compared to the first reactor design it was necessary to calculate the liner thickness after the tube shaping process.

The starting point was set by the PTFE-TFM tubing with 1.6 mm o.d. and 0.75 mm i.d. During heating and pressure increase the tubing stretched to an o.d. of 2.2 mm defined by the titanium tubing. To calculate the final i.d., it is necessary to calculate the cross section of the tubing, as the amount of material would not change. Knowing the cross section and the final o.d., the shaped i.d. and therefore the wall thickness can be determined. A direct determination after the shaping process by cutting the lined tubing and do an optical measurement was not possible. The cold and depressurized tubing shrunk always back to almost the original dimension.

The cross section had already been calculated in chapter 4.4.3:

$$CS_{PTFE} = \frac{\mathrm{o.d.}_{\mathrm{Liner}}^{\ 2} \cdot \pi}{4} - \frac{\mathrm{i.d.}_{\mathrm{Liner}}^{\ 2} \cdot \pi}{4} = 1.57\ \mathrm{mm}^2$$

After the shaping process, the PTFE-TFM tube completely fills out the supporting titanium capillary, therefor $\mathrm{o.d.}_{\mathrm{Liner\ shaped}} = \mathrm{i.d.}_{\mathrm{Titan}} = 2.2$ mm. The final $\mathrm{i.d.}_{\mathrm{Liner\ shaped}}$ can be determined with the help of following calculation:

$$\mathrm{i.d.}_{\mathrm{Liner\ shaped}} = \sqrt{\frac{\left(\frac{\mathrm{o.d.}_{\mathrm{Liner\ shaped}}^{\ 2} \cdot \pi}{4} - CS_{PTFE}\right) \cdot 4}{\pi}} = 1.68\ \mathrm{mm}$$

$$s_{\mathrm{Liner\ shaped}} = \frac{\mathrm{o.d.}_{\mathrm{Liner\ shaped}} - \mathrm{i.d.}_{\mathrm{Liner\ shaped}}}{2} = 0.26\ \mathrm{mm}$$

$s_{\mathrm{Liner\ shaped}}$ . . . wall thickness of the shaped liner

The new liner should have a similar i.d. as the old version after the shaping process, therefore the tubing was ordered with following properties:

Material: PTFE-TFM o.d. = 2.1 mm i.d. = 1.6 mm

The new cross section for the new liner tubing is 1.45 mm according to the formula above. After the shaping process, the i.d. will increase from 1.6 mm to 1.72 mm, meaning that the liner thickness was reduced from 0.26 to 0.23 mm. This small reduction did not negatively influence the stability. As the liner is shaped more homogeneously, it will protect the metal capillary equally on all positions. The previously used tubing was not always shaped concentrically giving areas with thinner and thicker walls. It was not possible to guarantee the tubing was stretched at equal rates all over the length and diameter. The effect of more stretching on one side can be seen in Fig. 4 - 18.

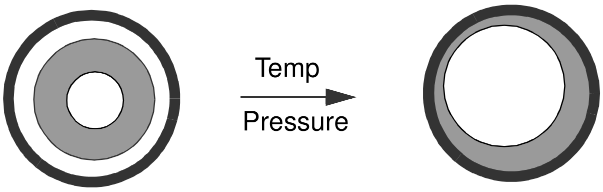


Fig. 4 - 18 Non-concentric tube shaping process

Using the new and larger liner it is not necessary to run such strong stretching, therefore the change of wall thickness is, even in the case of single sided expansion, unremarkable smaller compared to the basic design. To overcome the small gap between liner and supporting capillary, minimal reductions in the thickness of the wall are necessary.The new configuration is shown in Fig. 4 - 19.

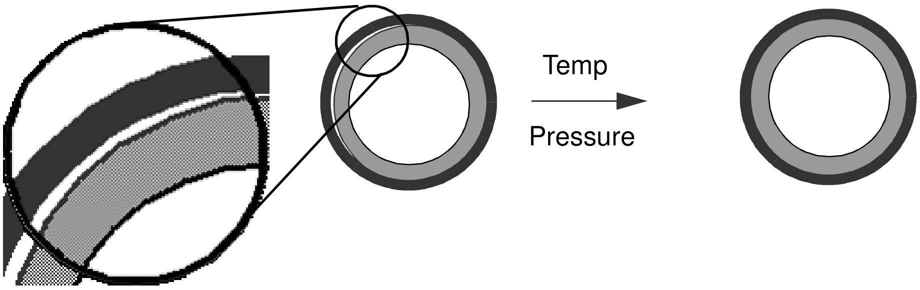


Fig. 4 - 19 New liner before and after the stretching process

Furthermore, the larger starting diameter made it necessary to adapt the fittings used in the system. The used standard fittings for 1.6 mm tubings had enough material reserve to be adapted to 2.2 mm tubing, which was achieved in Anton Paar’s machine shop. They used standard 1/16” connection fittings and increased the tubing receptacle on one side. The modified black adapter fitting can be seen between the reactor fitting and the tubing guiding the sample to the backpressure regulation valve in Fig. 4 - 17.

4.11 Conclusion

In summary the modifications and optimizations gave finally a reactor design fulfilling the needs specified at the beginning of this chapter:

- chemically inert material
  PTFE-TFM-liner in a titanium tube

- no or limited metal contaminations
  reduced trace metals in the supporting tube and metal free fittings

- high temperature stability
  permanent operation at 300℃

- high pressure stability
  working pressure of 150bar, short time pressure stability of up to 220 bar

- compatible with standard flow components
  Connection to 1/16'' tubings and valves

- inexpensive
  production costs of less than 50€ / reactor

- available in variable lengths
  with standard tubing minimum 5 m lined tubings are available

Based on this results the main component for a new digestion system was available.

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5 Development of an automated high performance flow digestion system

The newly designed lined reactor was designated as the heart piece of an automated digestion system. The lined tubing fulfilled all needs for sample preparation and determination of trace elements of liquid samples and slurries.

In addition to the main task, the decomposition of sample material using oxidizing reagents, the new equipment should also take over other sample preparation routine tasks. It should automatically take samples from an autosampler or an other sample source like a filter. Furthermore, the samples should be mixed with reagents and standards and collect a well defined amount after the process. If necessary, the final solution should also be diluted to avoid additional handling for the laboratory personnel.

Compared to other batch-loaded sample preparation systems, the flow digestion offers fast access to one single sample due to its highly efficient digestion process. The short preparation time can be used to continuously analyze a sample stream when a spectrometer is used instead of a collection autosampler after the process. In such a configuration, it should be possible to get analytical results 5 to 10 minutes after sampling. No other sample preparation technique for trace analysis can offer comparably short process times for one single sample. The combination of flow digestion and measurement asks for a synchronization between the different steps, as depending on the technique, different process times need to be adjusted to each other. Finally, it should be possible to run the system unattended for at-line analysis at least for a week to give detailed information of the sample composition for varying samples like mixed industrial and also for municipal waste water.

5.1 Basic flowchart for the valve-, pump- and sensor-design

Previously described systems mainly worked with simple peristaltic pumps to mix samples and reagents at a mixing point. The disadvantage of bad decomposition due to dilution by the carrier at the ends of the sample and acid plug have already been discussed in chapter 3.1. This problem can be overcome by using the loop in loop technique as shown by Berndt for example, but this design does not allow changes in configurations without changing the tubings.

Another problem is the precision of the peristaltic pumps, especially if concentrated acids need to be transported as the tubings will wear faster, loosing dosing precision. Therefore, the decision was made for dosing pumps in combination with distribution valves which allowed for a very flexible and precise mixing of sample, acid and reagent.

To control the process efficiently at least the reactor temperature and pressure need to be measured and controlled. Furthermore, monitoring the filling level of the carrier as well as the waste container helps to avoid interruptions due to missing or spilled reagents. Capacitive sensors can be comfortably used for that application avoiding direct contact of reagent and sensors.

The flow chart for the flow digestion system can be seen in Fig. 5 - 1.

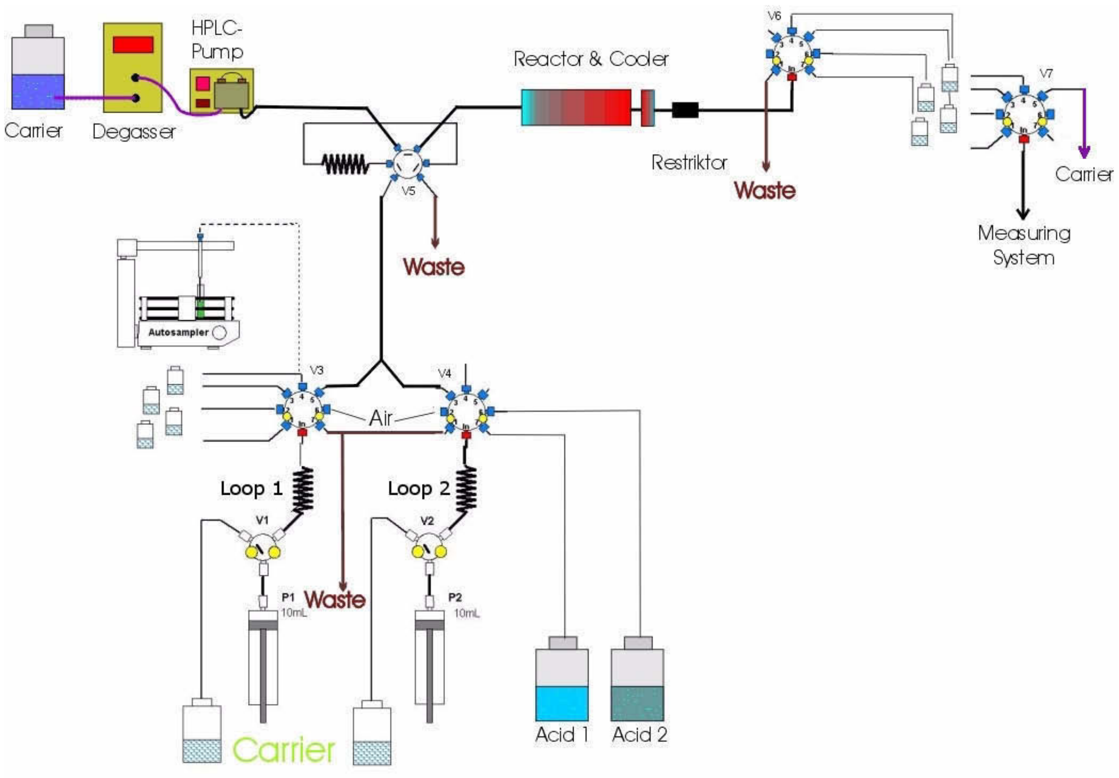

Fig. 5 - 1 Flow chart for an automated digestion system

High pressure section:

The pressure is produced with the help of a high pressure double piston pump and supplied via a degasser from a container with diluted nitric acid (3-5 % HNO_3 in water). The degasser is needed to remove dissolved air coming from the mixing procedure from the carrier. The injection valve V5 is needed to bring the sample and reagent mixture into the high pressure stream heading to the high temperature and pressure reactor. Beside the reactor and air cooler a restrictor valve is needed to set the pressure within the reaction system. The cool and expanded solutions are then distributed with the help of a multiport valve to different collection vials or an autosampler. Between the samples or in standby the stream needs to be directed to the waste. Not shown in the diagram is a pressure sensor between pump and injection valve as well as a temperature sensor inside the reactor which controls the reaction conditions.

Reagent handling section:

The sampling valves are designed to mix samples and reagents in varying compositions. Within the reagent handling section following liquid handling devices can be found:

Two piston pumps with a two port switching valve and 10 mL syringes:
pump one (P1) with valve one (V1) as well as pump two (P2) and valve two (V2))

Two sample loops:
Loop 1 and Loop 2 made of 1/8'' PFA tubing on a loop holder

Two low pressure multiport distribution valves:
V3 and V4

One high pressure injection valve:
6-port/ 3-channel valve made of PEEK to avoid metal parts (also part of the high pressure section)

One autosampler to supply samples to the sample valve V3

One tube connector in T-shape used as mixing-T for samples and reagents.

Sample collection section:

This section will collect samples in vials that are mounted in the section or via a separate port of the collection valve (V6) it can also bring the solutions to an autosampler (not shown). Another distribution valve (V7) in the collection area has tubings in all collection vials, allowing for the independent uptake of samples from the vials which are connected to a measuring device. The collection and the sampling valve (V6 and V7) are similar to the valves used for the regent handling with one central port and at least 6 connection ports.

5.2 Working principle of the automated flow digestion system

5.2.1 System startup

After filling and connecting all containers to the corresponding ports of the valves, it is necessary to fill the system with carrier solution for the first startup. All lines are rinsed with carrier except for the ports of the standards and acids. As carrier a very diluted nitric acid solution with typically 3-4 % is used to keep the system clean and acidic.

Filling the reagent handling system:
The reagent handling system is filled with carrier via the two 2-port valves (V1 and V2) mounted on the two dosing pumps (P1 and P2). The pumps take up carrier on the port connected to the carrier container and purges both sample loops (Loop 1 and 2). From there the carrier continues to the central port of the distribution valve for samples (V3) and to the valve for acids and internal standards (V4) respectively.
One port on each distribution valve is connected to the mixing-T. The carrier leaving valves V3 and V4 flows to the high pressure valve (V5) via these ports and fills the high pressure sample loop. Surplus carrier will be spilled to the waste via the waste port on valve 5.

Filling of the reagent lines:
The next step is filling all reagent lines that are connected to the additional ports of the sample (V3) and acid (V4) valve. To avoid contamination or dilution of the reagents the pump takes up first a small air bubble on one open port first, then the valve will switch to the first port that needs to be rinsed. The pump takes up a full stroke into the corresponding sampling loop. This loop needs to be larger than the pump volume to avoid reagents coming to the valve or pump. That is why it is not necessary to clean or replace the valve or pump unit regularly as the reagents will only contact the tubing of the loop.
After switching to the waste port of the connected valve the pump dispenses the solution and the air bubble to waste. To avoid that remaining solution stays in the system, the valve on the pump switches to the carrier and takes up a small amount of additional carrier. After returning to the position heading to the distribution valve the rinsing solution purges the sample loop and the valve. That means the loop is every time rinsed with a later amount of carrier than the amount of reagent that is taken up. This will help to avoid remaining acids or sample coming slowly closer to the valves V1 and V2 or even into the pump. For the acid ports, a small portion of typically additionally 50 µL carrier is pushed heading to the acid port itself to remove the concentrated reagent out of the valve to avoid corrosion of the valve.

Finally, the system will take up water to rinse the backflush ports of the high pressure pump. The pump therefore has two rinsing ports: one is connected to a water container, the other one is connected to one of the ports on the sample valve. After switching the valve V3 to the backflush port the pump P1 takes up water to rinse the pump. This procedure needs to be repeated regularly to keep the pistons of the pump rinsed.

A completely dry system is filled with air, therefore it is necessary to repeat all pump steps until the summarized pumped volume is larger than the connection tubing volume from the containers to the valve. After finalizing all needed ports the system will again rinse the loops and the connection from the sample- and acid-valve V3 and V4 to the injection valve V5 with carrier.

Start up the high pressure section:
The high pressure pump normally is able to start without manual filling, but with a carrier container standing under the table it did not work out properly. To overcome this problem a syringe was connected to the tubing leading from the pump to the injection valve. The syringe was able to prime the pump and after reconnecting the tubing to the valve the system could be started automatically.

To allow smooth tube shaping conditions the system first only increases the pressure to 30 or 40 bar, then the pump stops and the reactor core heats the filled reactor up to a temperature of 220℃. This is the temperature recommended by the manufacturer of the tubings (Elring Klinger, Dettingen, Germany). The same temperatures are used during thermal shaping processes for other PTFE parts at their site. Elevated temperatures soften the tubing to allow homogeneous blow shaping.

After reaching the limit of 220℃ the pump starts again at low pump rates to shape the thinner liner to the wider supporting titanium tube. The shaping takes place in the range of 80 to 100 bar. As soon as the liner has the final dimension the pressure increases further to the adjusted regulation value of approximately 150 bar. To avoid too much temperature removal during the further heating process the pump is run at low intensity. After having reached the final temperature the system is ready to start with samples. To safe carrier and reduce waste the system keeps a low pump rate until the first sample is in the queue.

5.2.2 Reagent mixing

The system is able to run three different processes. The main process is the digestion of samples, a variation of it is the digestion of a control sample, which means that instead of a real sample, a QC solution is processed. For the blank sample only the acid that is normally used in addition to the samples is send through the system to determine the possible contamination of the system. The general process is always the same, therefore the digestion of a real sample will be described in detail and after that, only the differences for the quality control sample (QC-sample) and the blank will be highlighted.

Sample uptake:

The first step is to rinse the sample line from the source (container, filter or autosampler) to the valve as it is still filled with air (first start) or with the previous sample. As first part of every pump stroke the system takes up a small air bubble (50-100 µL) from the air port on V3 to separate the sample from the carrier in the loop. Next the pump will take at least the volume of the connection tubing, maximally the highest possible amount for the syringe. Then the sample valve V3 will switch to the waste port to drain the content in the loop to waste. After that the pump valve V1 will switch to the carrier and take up approximately 100-200 µL carrier to push out the remaining sample using additional carrier. Together with the rest of the sample the separating air bubble will also be removed from the loop.

If the volume of the syringe is smaller than the volume of the connection tube these steps need to be repeated until the tubing is rinsed completely!

Reagent uptake:

The next step is to take up reagents and samples according to the chosen method. In addition to the separating air bubble, the sample pump also takes up other liquid which is needed to fill the dead volume of the tubings between the sample and injection valve. Normally twice the tube volume of the connection between mixing-T and the sample valve is efficient.

For the acid valve the mixing procedure is more complex compared to the sample valve. First it is necessary to take up an air bubble, then the first acid plug separating the sample/acid-mixture from the carrier in the sample loop is taken. Next, 50% of the control standard needs to be added. After that the system will take up the acid needed for digestion. It is simple when only one acid or reagent mixture is needed, but if two reacting reagents are needed the system must prepare this mixtures before the mixing process. This will be necessary, when the mixtures are not stable over a longer period of time. For example, the mixture of HNO_3 and HCl will produce gas bubbles according to following reaction:

$$HNO_3\text{(aq)} + 3\ \text{HCl (aq)} \rightarrow \text{NOCl (g)} + \text{Cl}_2\text{(g)} + 2\text{H}_2\text{O (l)}$$

Gaseous products mean difficulties for precise dosing of the reagents as the bubbles will change volume during the two dosing steps. During suction they are larger, but while pressing them into the sample loop they are smaller. In addition to that bubbles in the sample loop will have another dangerous side-effect: when switching the injection valve from the load position to inject the pressurized solution in the reactor will immediately expand into a partially filled loop. In case of too many bubbles in the sampling loop hot reagents may expand from the reactor into the PEEK tubing. This hot reagent may then causing thermal destruction and venting of the system.

The difficulties mentioned above explain why it is necessary to prepare the mixture only a few seconds before adding it to the sample to avoid gas production. The mixing will take place during the uptake of the reagent into the acid loop on acid valve V3. Depending on the settings the valve will switch between the different ports to mix the reagents. When two reagents are sequentially mixed in one hose the reagents need to be added in small fractions. The smaller the fraction is the better it is for homogeneous mixing, but portions of 100 to 200 µL have shown to be acceptable.

The mixing process of the acids starts with the obligatory air bubble and the acid plug which is needed to separate the sample from the carrier. As this plug will later be the last part of the mixing process with the sample it needs to be extended with the tube volume from sample valve V3 to injection valve V5. This guarantees that the plug will reach the injection loop completely while the additional volume will stay in the connection tubing. The next step is to take up 50% of the defined control or internal standard is. This will help to identify later the appropriate collection timing. Only if 100 % recovery for this internal standard solution is found the collection window was set properly. The process continues with the actual acid mixing shown in detail in Fig. 5 - 2. The figure includes the first steps ((step a) and step b)) for the acid plug and control standard as well as the final control standard and acid plug.

The first fraction is the main acid which is the same as is used for the acid plug. After taking up the calculated amount (see Fig. 5 - 2, c), the pump stops, waits for a certain period of time for pressure equilibration and then the valve V3 changes the port position to the port of acid 2 (see Fig. 5 - 2, d). There the first fraction of this reagent is taken up from the acid container before the valve switches back to the port of acid 1 (see Fig. 5 - 2, c) after the same waiting time as has been chosen for the first acid up-take. This cycle continues until the programmed acid is stored in the loop. Finally the system takes up the second fraction of the internal standard and closes the process by loading the final acid plug into the system (seeFig. 5 - 2, x).

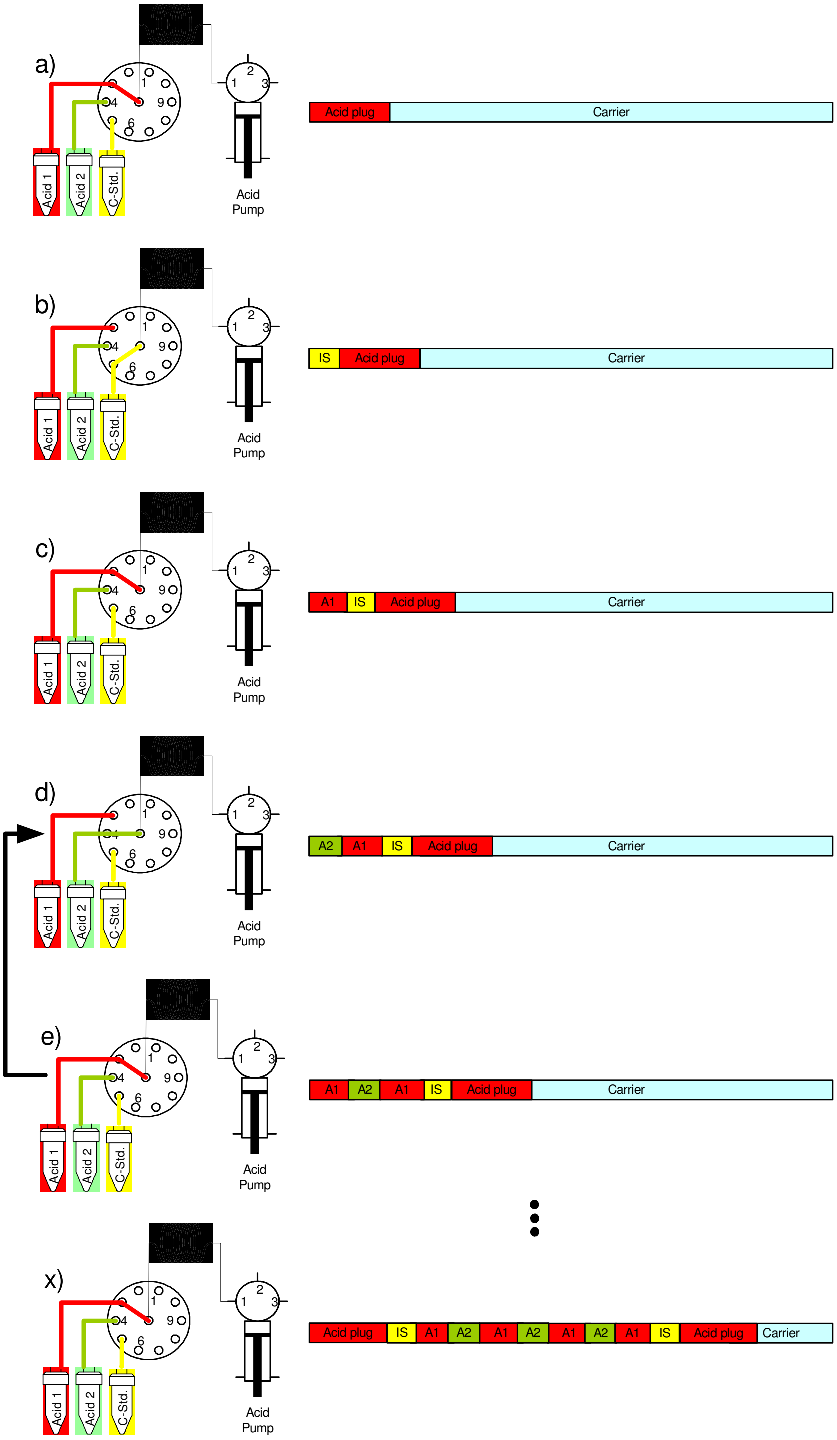

Fig. 5 - 2 Acid mixing process

5.2.3 Sample mixing

After the acid and the sample are taken into the sample and acid loops the injection valve will switch into the load position (see Fig. 5 - 3). Now the system can start to load the injection loop with the reagents and sample/acid mixture.

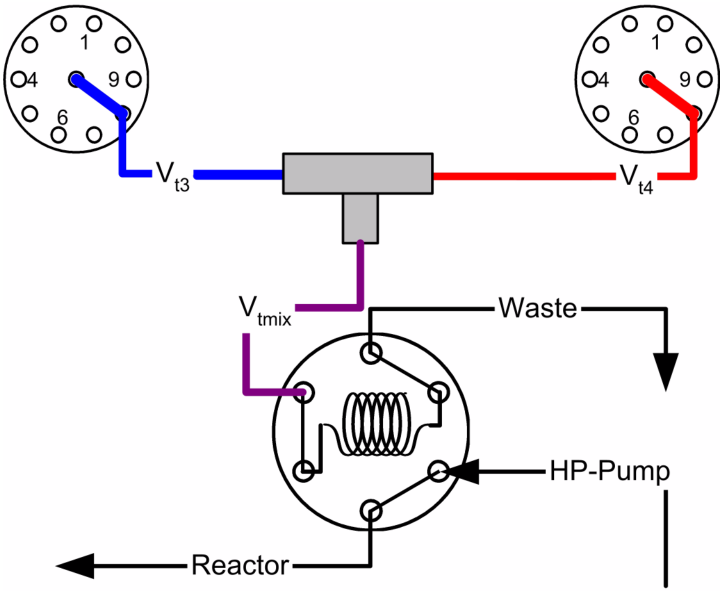

Fig. 5 - 3 Valve positions for the sample mixing step

The first step is to fill the connection between the sample valve and the mixing-T with sample. The needed amount is the dead volume V_{t3}. Within the next step the acid pump will load the acid plug and the control standard into the injection loop. The system adds the dead volume of the connection tubing between the acid valve and the mixing-T junction V_{t4}. This has to be done because otherwise the control standard would not pass the mixing-T which is necessary to bring the internal standard behind the other reagents. The most important step now is the mixing of the acids and the sample. Different amounts mean that different dosing speeds of both pumps. They should start and stop at the same time but need different speeds if the amounts are different. After that step the acid pump will continue with the second part of the control standard and the acid plug after the sample. The process closes with the addition of the dead volume V_{t4} and V_{tmix} to bring the mixture completely into the injection loop. Without that additional amount a part of the acid plug would partially remain in the connection tubing. The carrier in the loop, loaded with the HP-pump, will be drained to the waste during the filling process.

5.2.4 Sample digestion and collection

When all reagents finally are in the loop it is necessary to switch the valve to inject position as soon as possible. This is necessary to avoid that sample is pushed out of the system via the waste port due to the starting chemical reaction. The inject position will bring the sample into the hot and pressurized reactor (see Fig. 5 - 4).

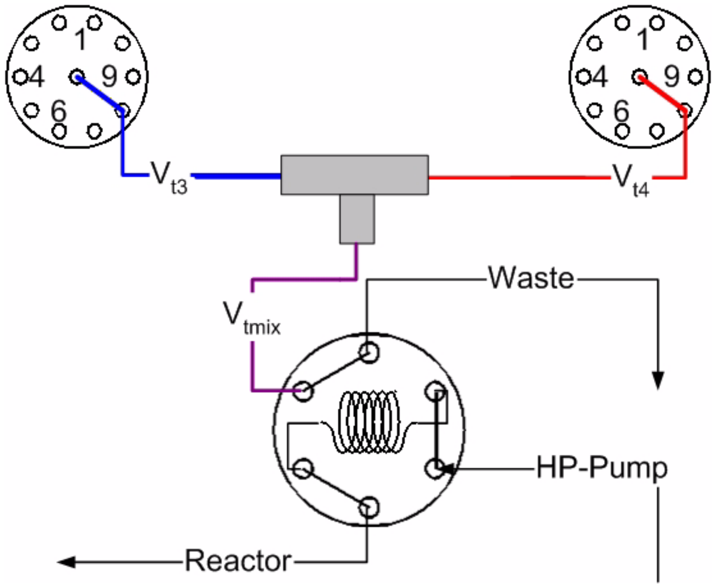

Fig. 5 - 4 Valve position for sample injection

As soon as the inject valve has been activated a counter starts which is waiting that the collection valve is switched to the collection position. The starting point of collection can be set to a certain time after the injection and may vary as a function of flow rate, sample size and the reactor volume. Theoretically the retention time through the reactor can be calculated according to following formula:

$$t_{retention} = \frac{\text{Vreactor [mL]}}{\text{flowrate [mL/min]}}$$

Due to non ideal flow and faster release the collection needs to start remarkably earlier and stop later than the theoretical time in the reactor. Only a wider collection window assure that the complete sample is collected. The reaction may push the sample faster through the system than the theoretical speed. This effect is stronger with high organic sample material in the solution. In addition to the front part of the sample plug, which is pushed faster through the system, another part of the sample and acid will also need longer than theoretically calculated.

Experiments for example have shown that 5 mL sample and 2.5 mL reagents will be collected safely within a collection window of 15 to 20 mL for a configuration with a 8 mL loop and a 10 mL reactor. The collection for this configuration should start 90 to 120 seconds after the injection of the sample in the high pressure system by switching valve V6 from the waste to the corresponding port of the collection vial. For 15 mL and a flow rate of 2.5 mL/min the collection will last 6 minutes, for 20 mL 8 minutes. The more reactive the sample the wider the sample spreads in the reactor. This means that the needed amount of collected sample may have to be increased corresponding to the organic content in the sample.

5.2.5 Cleaning and rinsing

During the digestion and collection time the sample preparation unit needs to be rinsed and cleaned before the next sample. Depending on the analytical needs this step can be done in different intensities. Minimum is that both loops are rinsed with carrier coming from pump P1 and P2 respectively. The acid and sample valves still remain in the position heading to the mixing-T. Therefore not only the loops and valves are rinsed, but the connection to the injection loop is also cleaned. The rinsing solution will be drained on the waste port of the injection valve. Depending on analytical needs a cleaner solution can be taken up on one port of the sample valve V3 to clean the loop, the mixing-T and the corresponding tubings. A solution of metal-free lab cleaning agent can be used for that purpose. After that step it is necessary to rinse the cleaned tubing with carrier again similar to the first step of the whole procedure.

The injection loop on the injection valve will be rinsed and cleaned by the high pressure carrier stream. A cleaning step before filling is possible, but was not used during the experiments.

The sample tubing of the sample source will be cleaned with the help of the next sample. Rinsing with a detergent would be possible, but was not applied during the experiments as the sample concentrations were not varying too much.

5.2.6 Control standards and blanks

Control standards or regular blanks allow to determine the performance and status of the instrument. Losses during the sample preparation process due to wrong settings of the collection time for example could be seen with the control standard. Leaks in the system or adsorption on contaminated tubing surfaces would also lead to lower recoveries.

A sample blank on the other hand would provide information about the cleaning status of the tubings and the reactor. Contaminations or inefficient cleaning cycles can be detected by too high blank levels of the system. The used fluoropolymers tend to take up contaminants due to the porosity of the material and can give information about the general condition of the reactor.

The control standard will run similar to a normal sample with the difference that the system takes up the sample from a different port of the sample valve V3 and that the pre-rinsing of the connection tubing is cancelled as this port is always filled with the same liquid. The rest of the process is identical with a normal sample preparation step.

No sample or control standard is needed for the blank. Only the reagents prepared by the acid valve. Acid 1 and acid 2 respectively as well as the internal standard are injected in the system to determine the contamination status of the tubings and the reactor.

5.2.7 Measurement of collected samples

Once the samples are collected the system is ready to measure them by using spectroscopic techniques like AAS, ICP-OES or similar ones. The control software can provide the solution to such instruments now by switching the sampling valve V7. Every port of this valve is connected to one collection vial with a conical bottom. This will provide the solution to the measuring devices with the help of their included pumps (for ICP-instruments) or an additional peristaltic pump for AAS systems. For AAS the pump is necessary to minimize the effects of different tubing lengths to the spray rate of the nebulizer. The collection vials need to have three ports: one for the sample-in tubing, another one for releasing the fumes which will escape at the end of the tubing and result from the chemical reaction (see bubbles in Fig. 5 - 5) and a third one to connect the vial with the sampling valve V7. The reaction gases also have the task to mix the different fractions of the sample solution in the vial to provide a homogenous solution.

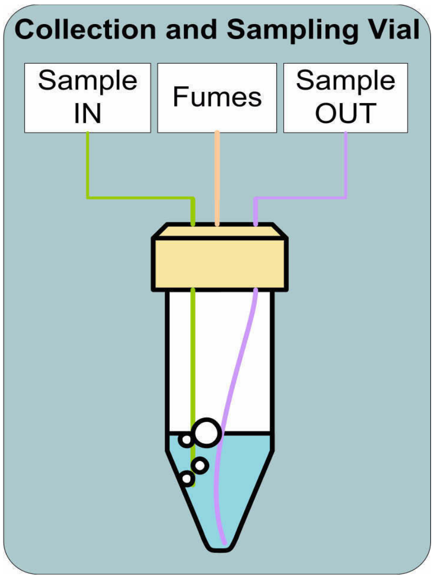

Fig. 5 - 5 Collection and sampling vial for the final solutions

After the determination is finished the vial needs to be drained before filling in the next sample. This can either be done by the sample pump of the measuring device or with an extra waste pump. The disadvantage of using, for example, the peristaltic pump of the ICP is the time needed for this step. Even in a purge mode it will take several minutes to remove the remaining approximately 10 mL after the measurement. In such a case an additional pump in the sampling line (not shown in the flow chart Fig. 5 - 1) could help to speed up the process. Furthermore the plasma of the ICP is protected against the high sample load occurring during a purge mode and giving better stability. The working principle is shown in Fig. 5 - 6. The shown check valve is needed to avoid waste solution is drawn together with the measuring solution.

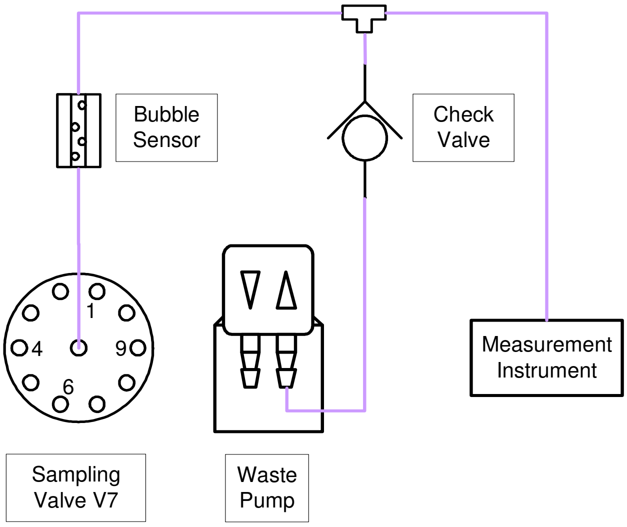

Fig. 5 - 6 Bubble sensor and waste pump for fast drainage of the collection vials.

An AAS system needs more for the determination of several elements and consumes higher amounts of reagents than an ICP. In such a case the instrument could be used to empty the vials and avoid the additional pump and valve.

Calibration solutions:

Depending on the numbers of the sample vials, calibration standards and ports on the sampling valve V7 it is possible to run the instrument calibration via this valve in two different modes.

Mode 1: The number of vials and standards is smaller or similar to the number of ports on V7
In addition to the collection vials the standard solution containers as well as the blank are also connected to the system. For calibration of the measuring device the flow digestion system needs to synchronize with the instrument's software to switch to the corresponding ports providing the needed calibration solutions.

Mode 2: The number of vials and standards is larger than the number of ports on V7
In such a configuration it is necessary to use an autosampler that provides the calibration solutions for the instrument. This sampler will then be connected to one port of the sampling valve which will be chosen while the measuring device is running the calibration. The autosampler needs to be controlled by the spectrometer control software.

5.3 Components and devices of the flow digestion system

While the flow chart and the processes of the flow digestion system have been described in the section before this chapter focuses on technical details. A list of all components used should be given including the product manufacturer and product type. Special features of the liquid handling devices as well as control sensors and µ-processor control units will be discussed. The focus will lie on electrical and electronic components as well as tubings and fittings. Standard components like cables, screws and housing are not part of this list. The reactor is also not a part of this collection as it is described in detail in chapter 4.9.

5.3.1 High pressure components

High pressure pump
To build up pressure in the system a small two piston HP-pump (WellChrom K-120, Knauer, Berlin) with ceramic inlays was used. The maximum flow rate of the used pump is 10 mL, the working pressure up to 400 bar. The settings are controlled only via a serial RS-232 connection.

Injection valve
For the high pressure injection a 6 port / 3 channel PEEK valve for 1/16'' tubing was used including an electrical valve drive (valve and drive K6, both Knauer, Berlin). The drive was also controlled with the help of a digital signal from the programmable controller to change from load to inject and vice versa.

Back pressure regulator
In addition to reactor and cooler a commercial backpressure regulator made of PEEK and a fluoroelastomer sealing were used (P-880 Upchurch-Scientific, Oak Harbor). As the sealing membrane

disintegrated after s few days because of the contact with higher concentrated acids it was replaced by a combined higher resistant fluoroelastomer membrane. This membrane was made of Kalrez and covered additionally with a PFA film. The new material enabled an operation of several weeks without interruption at a pressure of 140-180bar and at flow rates of typically 0.5 to 2.5 mL/min.

5.3.2 Sample handling devices

Dosing pump with valves for samples and reagents

In order to allow for precise reagent and sample mixing a high precision and chemical resistant pump and valve unit with a 3-port distribution valve were used (Cavro XL 3000, Tecan, San Jose, CA). The system can be applied with various different glass/PTFE syringes. The pump was made for high resolution dispension (24.000 steps/stroke) and used with 2.5 and 5 mL syringes.

Distribution valves

The distribution valves are 6 port valves with a common central port (SmartValve, Tecan Inc., San Jose, USA) allowing the connection of 1/8" and 1/16" tubings which use 1/4"-28 UNF flat bottom fittings (see chapter 5.3.4). The rotating body is made of PTFE, the stator of Kel-F. The stator itself is fixed in an aluminium body which also contains the threads for the fittings. A stepper motor is turning the valve to the programmed port. The unit can be controlled by the serial protocol RS-232 or RS-485.

5.3.3 Sensors and controller

Temperature sensor

The reactor was heated by a 100 W and 24 V heating cartridge controlled with the help of a Pt100 temperature sensor with a precision of 1 %. The sensor was installed in the heating cylinder together with the cartridge. A programmable controller (see below) had a build-in Pt100-sensor port allowing for the control of the reactor with the help of a temperature control routine.

High pressure sensor

The reactor pressure was controlled with the help of a load cell sensor which was installed in a holder between injection valve and high pressure pump. The sensor measures the pressure within a range of 0 to 350 bar with a precision of 1 % (Keller, Winterthur, Switzerland). The analog signal (4-20 mA) from the sensor is connected to an analog input port of the controller.

Bubble sensor

The connection to the ICP was under supervision of a bubble sensor detecting proper filling of the sampling tube and its main aim was to detect air after completely removing the solution from the collection and the sampling vial. The sensor was a prototype working on an optical principle. A light beam from a LED was beamed through an installed tubing at an angle of approximately 20 °. A detector at the other side, slightly shifted in position, only detects light if the tubing is filled with a liquid that has a higher optical refractive index. An empty tube shifts the light beam differently from a filled one which reduces the signal at the detector. The detector worked fast with different kinds of liquids, but the problem was that the sensor did also indicate liquid in form of only small droplets. The working principle as well as the malfunction situation can be seen in Fig. 5 - 7.

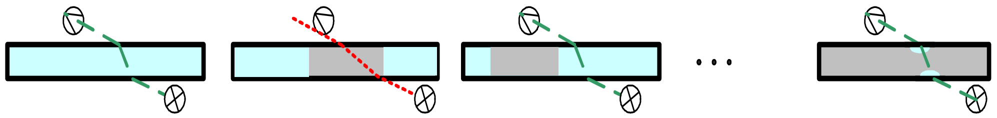

Fig. 5 - 7 Optical bubble sensor: Function and malfunction with droplets

Programmable controller and interfaces

For the control of the process a standard commercial programmable controller with corresponding modular interfaces was used. The reason for that approach was the availability of almost all kinds of interfaces which allowed for the easy extension of functionality by adding the modules needed. The included software supported PC update and monitoring. The chosen controller (Model 2003 7CP476.60, B&R Automation, Eggelsberg, Austria) offered with the basic module the CPU as well as one CAN and one serial RS-232 port. One optional extension module offered additional ports like RS-485 for the communication with the valves and LAN for the TCP/IP connection. Another module was used to read the analog pressure and temperature signals. The input module offered direct connection of two PT-100 temperature sensors for the reactor and the cooler sensor. A combined digital input/output unit completed the setup. The controller was supplied with the help of a 24 V and 20 A power supply which delivered enough power for all valve and pump drives as well as for the heating cartridge and the sensors.

5.3.4 Tubing and fittings

For the connection between the different valves and pumps in the low pressure section high purity PFA tubings were used. The material has extremely high chemical resistance and purity which prevents the contamination of the tubings. Two types were used: 1/16’’ o.d. (1.6 mm) with an i.d. of 0.75 mm as well as tubings with 1/8’’ o.d. (3.2 mm) and an i.d. of 1.5 mm (both from Upchurch Scientific, Oak Harbor) for sample and acid loops as well as the supply hoses to the pumps.

The high pressure connections as well as the injection loop are made of PEEK capillaries 1/16’’ o.d. (Upchurch Scientific, Oak Harbor) with an i.d. of 1.0 mm for the injection loop and 0.75 mm respectively for all other connections.

The PFA tubings were installed using flat bottom fittings which consisted of a ferrule either for 1/16’’ or 1/8’’ with the corresponding nut. The two versions can be used for all 1/4-28 flat-bottom threads in the valves and pumps. For the high pressure connections SealTight fittings were ordered consisting of a specially designed nut and PEEK polymer ferrule. This system grips at two compression points and can therefore hold tubing up to 620 bar, usually with just finger tightening (Upchurch Scientific, Oak Harbor). The fitting is designed for standard 10-32 conical ports and is shown in Fig. 5 - 8 together with the low pressure flat bottom fittings.

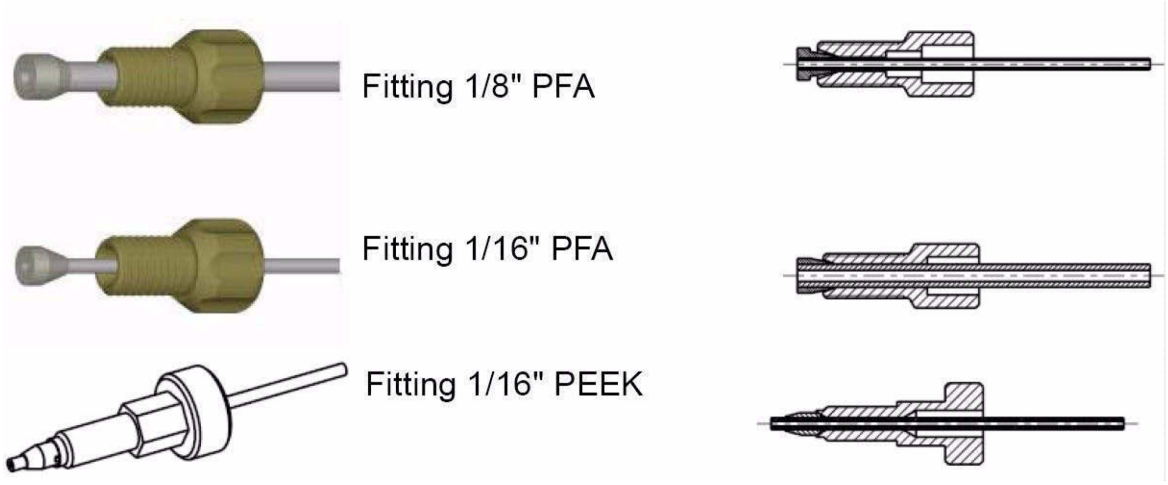

Fig. 5 - 8 Low pressure fittings for 1/16” and 1/8” made of PFA as well as a high pressure fittings made of PEEK

The special fitting which was used for the reactor design to fix the titanium tubing and the reactor liner have already been discussed in chapter 4.4.2. The standard superflangeless fitting came from Upchurch Scientific, Oak Harbor. The fitting with the conical junction and the drain was a development of Anton Paar, Graz.

5.3.5 Mechanical setup of the automated digestion system

For a safe and reliable operation the following prerequisites are have to be fulfilled:

- the electric/electronic components need to be separated from the liquid handling

- the pressurized components need to be covered to avoid acid spillage in case of a tubing failure
- movable parts need to be designed in a way that prevents injuries like cutting or squeezing
- the design should allow the easy access to all components for service and installation of add-on’s

To fulfill all needed requests a rack made of a modular system was developed which allowed for the installation of all components on laser cut stainless steel sheets. The closed body offered the necessary protection of the sensitive electronic components and in addition allowed the installation of a protection shield in front of the tubings and valves. In Fig. 5 - 9 the design of the system can be seen. More details are discussed in chapter 6.

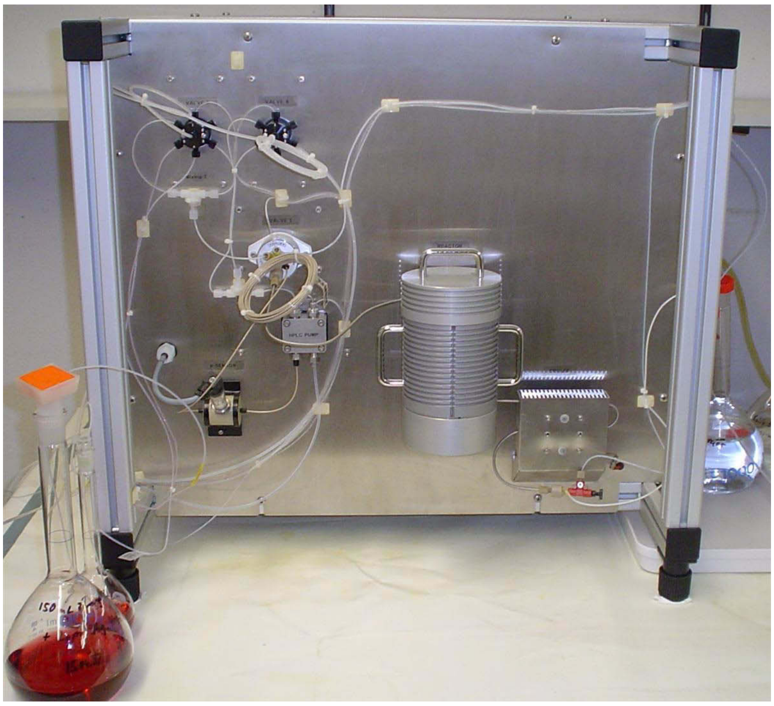

Fig. 5 - 9 Prototype setup for the automated flow digestion system

5.4 Process development and optimization

To get the best process conditions like collection start, collection volume and rinsing time the system was connected online to an ICP-OES to determine the retention times for different reaction conditions. For this special application a liquid/gas separator was used as interface between the ICP and the flow digestion system. Due to the extremely high temperature the carrier and digestion acid forms gaseous

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products like NO and NO_2. These gas bubbles would cause fluctuations of the nebulizer rate in case of direct coupling and lead to bad readings of the spectrometer. In addition to removing the bubbles an adjustment between the different flow rates of the digestion unit and the ICP nebulizer can be reached.

5.4.1 Online interface

The scheme of the online interface is shown in Fig. 5 - 10. The basic principle comes from the collection and sampling vials presented in chapter 5.2.7. An additional port in the vial is connected to a pump with higher flow rates. In this case the flow digestion system guarantees that the filling level in the tube does not exceed the end of the waste tubing. The adjustment of all tubings is close to the bottom of the conical vial to ensure minimum dead volume. The best positioning is shown in the picture: the inlet should be at the bottom mixing up the remaining and the new solution with help of the gas bubbles. The sample outtake tubing should be positioned slightly separate to avoid bubbles coming into the hose. Finally the waste tube will set the filling level and therefore needs to be installed a little bit higher than the two others. This setup will allow to see changes in the sample coming from the digestion system immediately.

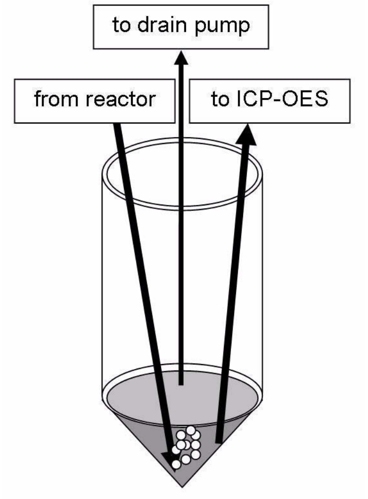


Fig. 5 - 10 Liquid-gas separator with additional waste connector to keep minimum dead volume

5.4.2 Determination of retention times using ICP measurement

With the separator described above even different flow rates between the digestion system and the ICP can be handled. The waste pump will keep a constant level as long as the flow rate of the digestion system is at least equal or higher than the ICP pump rate. Using the configuration shown it was possible to determine the retention time for flow rates between 0.5 and 2.5 mL/min from the flow digestion system keeping the ICP pump-rate at optimized ratings of about 1.0 mL/min.

The ICP-OES was equipped with a cross-flow nebulizer and a Ryton spray chamber (both Perkin Elmer, Shelton). The control software Winlab 32 allows to run online reading with on the fly changes of all plasma settings for up to 6 wavelengths at the same time. This function is intended for method development but can also be used to read-out transient signals. The disadvantage of that mode is the missing function for saving the signals. Therefore it was necessary to use a stop watch to note down the values manually for all investigated elements. The results allowed to determine optimized start and end points for the collection.

Experiments

For the investigations different solutions with elemental standards and organic samples spiked with standards were used. The experiments started with acidic solutions spiked with Sc and Ba, later on other elements were added. To see the influence of the digestion reaction on the retention time red wine was used as a sample. The applied Cabernet Sauvignon with 14% alcohol offering a mixture of easy and more difficult decomposable organic materials. The red wine was spiked with elemental standards.

Instrumentation: Optima 4300 Dual View (Perkin Elmer, Shelton)

Standard elements solutions: diluted from stock solution with 1000 mg/L of the needed element (CertiPUR, Merck, Darmstadt); USUALLY in HNO_3 5 %

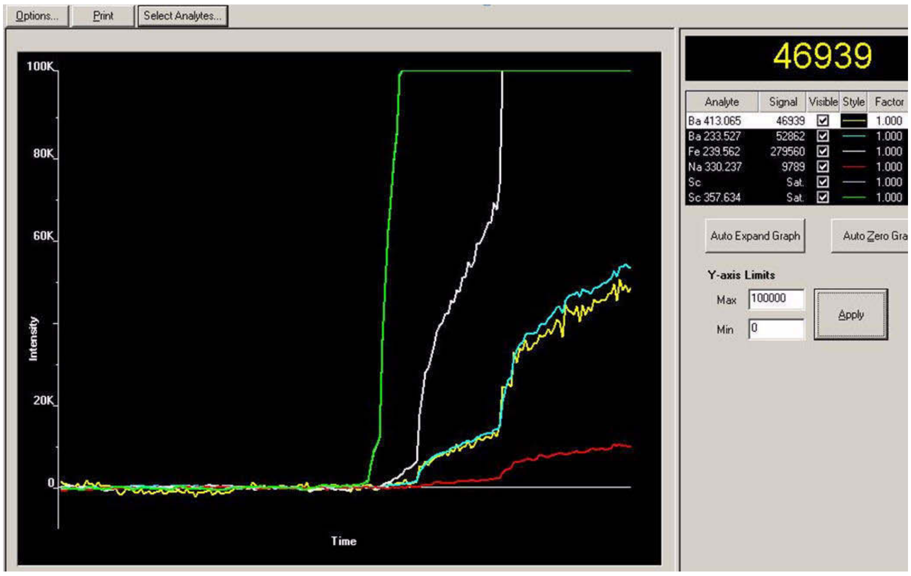
Water: >18 MOhm from the lab high purity water supply system

Acids: subboiling HNO_3 65%, produced according to the requirements just before use in the lab by applying a quartz distillery (Kürner, Rosenheim) using 65 % p.A. quality acid (Merck, Darmstadt).

To show how data were achieved first of all an experiment is explained which uses red wine as a sample. This sample was not the first in the row but only for this sample screenshots of the software are available to explain how the data were obtained in online mode. The screenshots are missing for the other experiments as only the values were noted down manually into a table.

Reaction conditions: Flow rate: 2.5 mL/min Reactor: 300 °C Pressure: 150 bar
Sample volume: 1.6 mL Acid volume: 2.2 mL (nitric acid 32.5%)
Spiked elements: Sc, Ba, Fe, Na, each with a concentration of 1 mg/L

For Sc and Ba two independent wavelengths were measured. The remaining two channels were used for one Fe and one Na wavelength. Four screenshots were made, each one with a different scaling for intensity. The maximum intensity was 100.000 (after 3:30 min), 1.000.000 (after 4:30 min), 2.000.000 (after 6:30 min) and finally 20.000 (after 7:30 min).

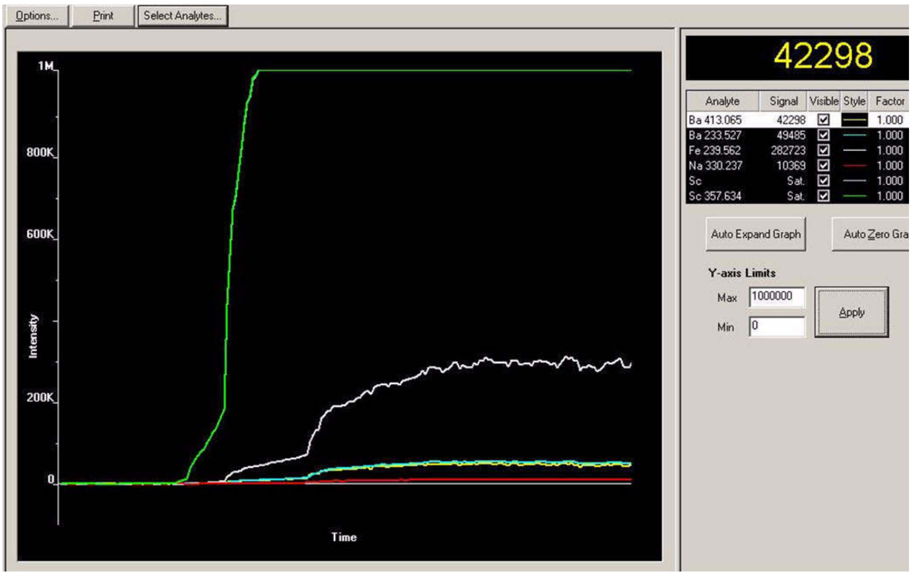


46939

Analyte	Signal	Visible	Style	Factor
Ba 413.065	46939	☑	—	1.000
Ba 233.527	52862	☑	—	1.000
Fe 239.562	279560	☑	—	1.000
Na 330.237	9789	☑	—	1.000
Sc	Sat.	☑	—	1.000
Sc 357.634	Sat.	☑	—	1.000

Y-axis Limits
Max 100000
Min 0

Fig. 5 - 11   Wine sample after 3:30 min: Sc lines are increasing completely parallel (scale: 100.000)



42298

Analyte	Signal	Visible	Style	Factor
Ba 413.065	42298	☑	—	1.000
Ba 233.527	49485	☑	—	1.000
Fe 239.562	282723	☑	—	1.000
Na 330.237	10369	☑	—	1.000
Sc	Sat.	☑	—	1.000
Sc 357.634	Sat.	☑	—	1.000

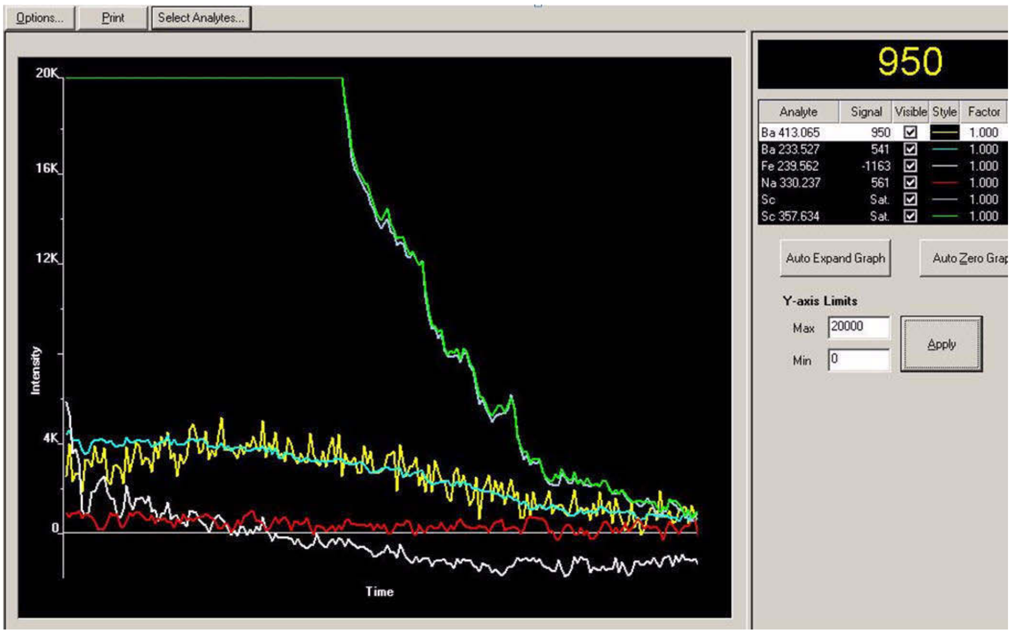
Y-axis Limits
Max 1000000
Min 0

Fig. 5 - 12   Wine sample after 4:30 min: concentrations are constant (scale: 1.000.000)

Analyte	Signal	Visible	Style	Factor
Ba 413.065	3005	☑	—	1.000
Ba 233.527	4002	☑	—	1.000
Fe 239.562	773	☑	—	1.000
Na 330.237	417	☑	—	1.000
Sc	Sat.	☑	—	1.000
Sc 357.634	Sat.	☑	—	1.000

Max 2000000
Min 0

Fig. 5 - 13   Wine sample after 6:30 min: decreasing signals. Sc lines are separated (scale: 2.000.000)



Analyte	Signal	Visible	Style	Factor
Ba 413.065	950	☑	—	1.000
Ba 233.527	541	☑	—	1.000
Fe 239.562	-1163	☑	—	1.000
Na 330.237	561	☑	—	1.000
Sc	Sat.	☑	—	1.000
Sc 357.634	Sat.	☑	—	1.000

Max 20000
Min 0

Fig. 5 - 14   Wine sample after 7:30 min: signals reaching the starting values again. (scale: 20.000)

As the time axis scale could not be changed in the software to display the whole collection in one window it was necessary to note down the intensity manually to get a diagram for the complete collection. The signals for the investigated elements of the experiment can be seen in Table 5.1.

Table 5.1: Intensity time table for 1.6 mL red wine sample, flow 2.5 mL/min

Time	Time cor.	Sc	Fe	Na	Ba
0:00	00:00	1	1	1	1
2:00	01:45	1	1	1	1
2:29	02:14	5000	1	1	1
2:37	02:22	1600000	2000	190	1000
5:30	05:15	800000	15000	1490	10000
6:00	05:45	25000	1500	643	5900
6:30	06:15	800000	773	417	4000
7:00	06:45	25000	383	643	5900
07:30	07:15	1000	1	560	540
8:00	07:45	110	1	88	75

The liquid-gas separator was installed as closely as possible to the ICP-OES instrument. Nevertheless the sample needed 15sec from the separation vial to the spray chamber at the chosen pump rate of 0.9 mL. The time for signal stabilization cannot be determined exactly due to mixing and delayed wash out effects in the spray chamber. Therefore the time table was corrected only for the delay caused by the connection tubing (see "Time corr."-column). Before the experiment the intensity counter had been set to zero and at the end of collection time the Fe-signal was below the start point (see screenshot Fig. 5 - 14). In order to be able to draw a logarithmic table the negative values were set to 1 (see grey boxes), the other values are as determined as you can see in Table 5.1.

In order to check the influence of the reactivity of a sample experiments were carried out with and without organic matrix in the sample solutions. To check the proper function of the online coupling additionally an offline measurement with fractionated collection was done.

The following diagrams show examples for determined retention time as function of the sample volume and the flow rate.

Retention time for online collection

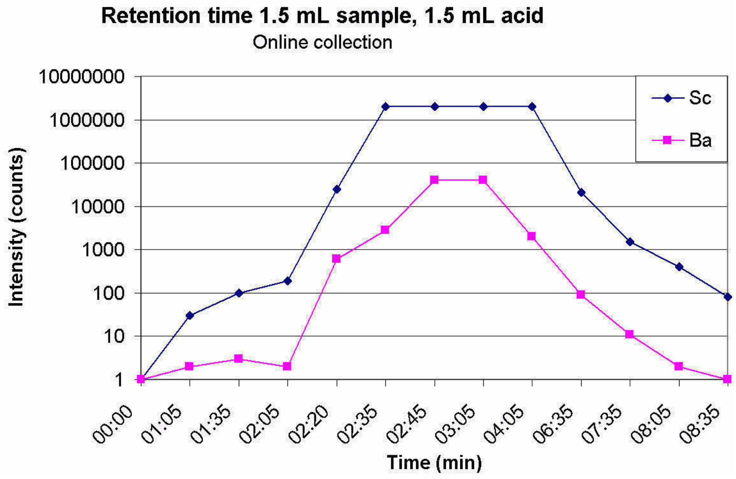


Fig. 5 - 15 Retention time: Flow 2.5 mL/min for 1.5 mL aqueous solution and 1.5 mL acid

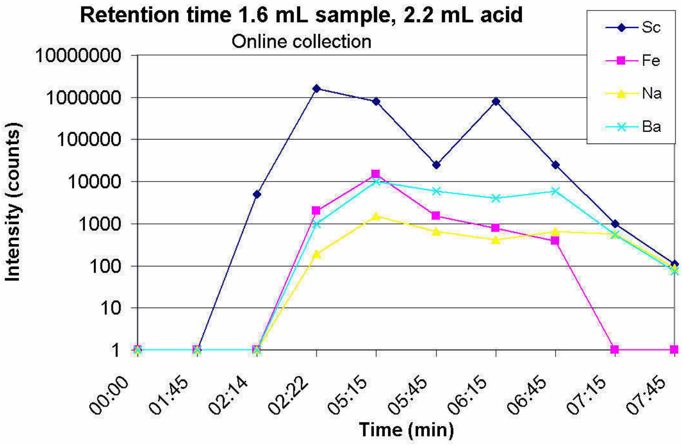


Fig. 5 - 16 Retention time: Flow 2.5 mL/min for 1.6 mL wine sample and 2.2 mL acid

Retention time for offline collection

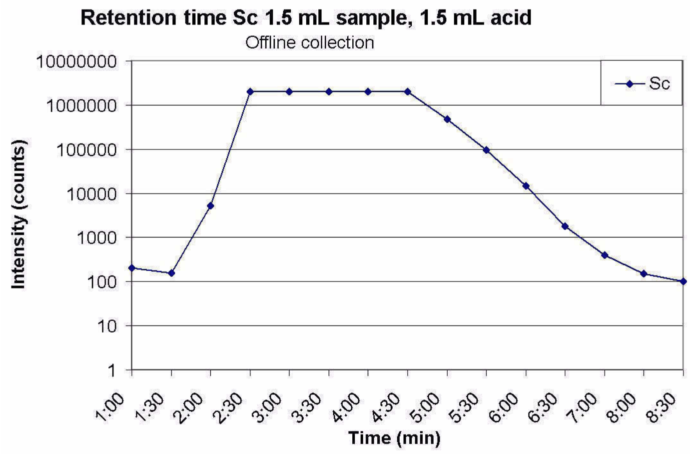


Fig. 5 - 17 Retention time: Fractionated collection, flow 2.5 mL/min for 1.5 mL sample and 1.5 mL acid

Conclusion:

Scandium seems to pass through the system faster than the rest of the elements but at the same time also remains longer than the others. The decrease of the Sc signal during the wine digestion is not shown in the screenshots above, but can be seen in the diagram of the collected intensity data. It appears that during the process different Sc species were separated inside the hot reactor tube. A possible explanation is the formation of different compounds, for example nitrate complexes. They may interact in different ways with the non-polar PTFE surface of the reactor compared to the Sc cations.

This behavior could be used to determine the completeness of the sample collection. Having a good recovery for Scandium all other elements should be within the collection window as well.

5.4.3 Determination of decomposition performance using TOC measurement

After the determination of optimized decomposition and collection parameters the performance of the new setup was investigated by using TOC measurement. As test solutions three different organic materials, which are known, were chosen: glucose, glycine and the most difficult one, nicotinic acid.

Water:	>18 MOhm from the lab high purity water supply system
HNO_3 65%	produced, according to the requirements just before use in the lab, applying a quartz distillery (Kürner, Rosenheim) using 65 % p.A. quality acid (Merck, Darmstadt, Germany).
Test materials:	Glucose, f. Biochemistry (Merck, Darmstadt, Germany) Glycine, f. Molecular Biology (Merck, Darmstadt, Germany) Nicotinic acid, purum (Sigma Aldrich, Munich, Germany)
TOC measurement:	Shimadzu TOC Analyzer 5060

An amount of 2.2 mL of a 1 % solution was mixed in the system with 2 mL of half concentrated (32.5 %) nitric acid and digested at a flow rate of 2.5 mL/min at 300℃ and a pressure of 150 bar. While glucose and glycine were decomposed the nicotinic acid did not dissolve. Even the reduction of the system's flow rate to 1.5 mL/min, and therefore a 66 % longer digestion time, did not change the efficiency. The results are compared with data received from the Autoflow system (26 m at a working pressure of 35 bar and different retention times.

Table 5.2: Remaining Carbon concentration after flow digestion

	Flow digestion system		**AutoFlow System**	
Sample	Remaining Organics (%)	Retention time (min)	Remaining Organics (%)	Retention time (min)
Glucose	4.3	4	6.0	4
			1.0	8
Glycine	10.1	4	38.0	4
			17.0	8
Nicotinic acid	~ 100	4		
Nicotinic acid	~ 100	6.6		

As can be seen in Table 5.2 the digestion performance is different between the two systems when 1:1 diluted HNO_3 is used. For glucose the results with 4 min retention time are comparable, with 8 min retention time in the Autoflow the digestion was even better. For glycine the digestion quality could be improved by expanding the reaction time from 4 to 8 minutes in the microwave system, too. Nevertheless the TOC values are two to four times higher compared to the high temperature reaction in the FDS. There are no data available about the nicotinic acid for the autoflow system.

The influence of H_2O_2, which was used to reduce the acid concentration in the digestion, was investigated in parallel by Pichler with the Autoflow. Small amounts did not improve the results, but higher concentrations of H_2O_2 remarkably decreased the performance. Therefore such mixtures were not investigated in the FDS experiments.

6 Effluents monitoring container for trace metals

6.1 Requested features and functions

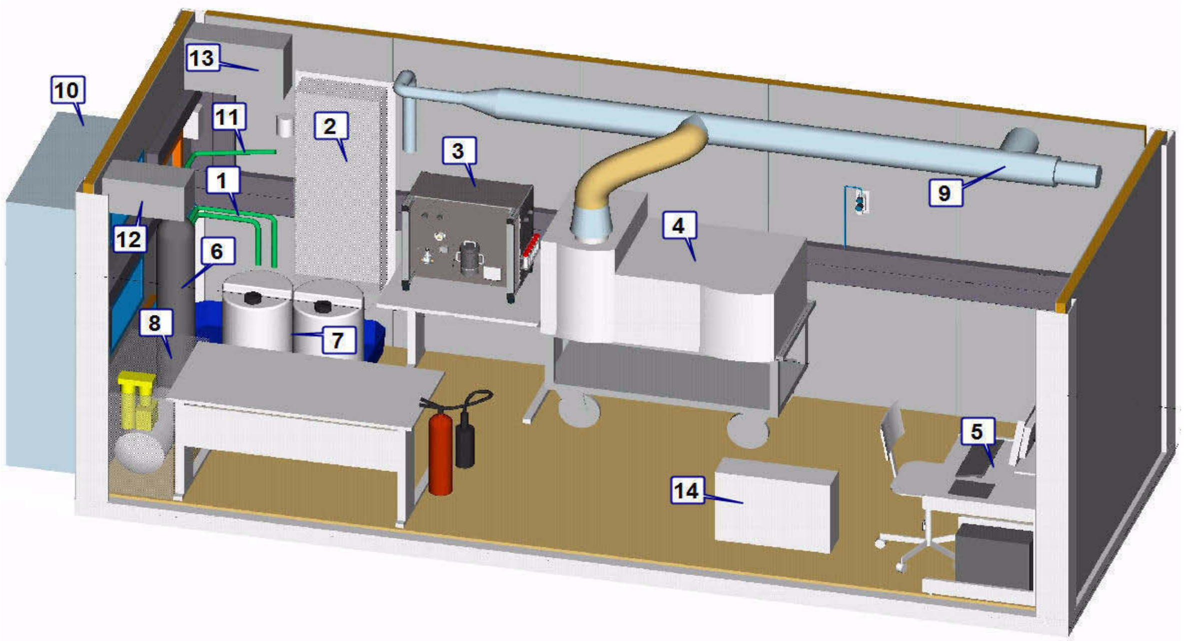
The possibility to run fully automated sample preparation and measurement raised the interest for a system that is capable to monitor effluents unattended from several days up to one week. In addition to the digestion with acid this would also require measuring devices like ICP- or AAS-instruments. In case of too large particles in the sample streams filters and supply pumps are needed. Sample preparation and measuring equipments also require supply systems for the reagents, gases and the waste. As depending on the place of installation, environmental conditions can be severe protection against dust and high or low temperature must be provided. A powerful monitoring and data processing system, connected to the remote control lab, is required. The monitoring allows to forward the analytical data gained and to manipulate and supervise the reaction conditions. The same system should also provide the necessary error handling. Furthermore it is necessary to protect the operator and the environment against hazards coming from the used gases and the extreme reaction conditions with pressurized hot acids.

In order to verify the performance of the flow digestion system in process environment it was necessary to design and build a system that offers all the needed infrastructure mentioned above. Finally this configuration needed to be tested on an industrial site to indicate performance as well as forgotten design weaknesses.

6.2 Container components

The goal of the experiments was to set up a system which is ready to run 2 4h for 7 days without interruption or service needed. It should run an analysis of 10 to 15 elements fully automated every 8 to 10 min in a feed waste water stream. To avoid dependency on local prerequisites the system should be installed in a container offering air condition, heating, reagent supply and waste collection. Furthermore it was necessary to include inlet filters and exhaust systems, argon gas supply and electric as well as computer network infrastructure. In addition to the work benches for the instruments space for service and standard solution preparation were necessary. On a separate desk space needed to be reserved for the control PC for the complete system. For easy installation of the complete container a filtration unit, which was needed for the prefiltration of heavy polluted samples, should be included as well. Finally it was necessary to add the needed safety precautions to avoid dangerous atmosphere in the container in case of an argon leak or the breakdown of the exhaust system in the small container. The collection of leaking reagents or waste due to overfilling of the collection containers has to be monitored and connected to a safety switch-off to prevent acid and waste spillage in the container or the installation site.

In Fig. 6 - 1 a principal scheme of the necessary setup is shown. All mentioned features and components are placed in a way that reduces the length of connection lines and allows easy and safe service and operation. Not shown in the drawing are two bundles of argon bottles outside the container to supply the ICP for at least 1 week without interruption.



Pos.	Component	Pos.	Component
1	sample supply tubing	8	compressor
2	filter unit	9	exhaust system
3	flow digestion unit	10	air condition
4	spectrometer	11	waste & drain
5	computer	12	air inlet filter
6	argon supply	13	electric switch box
7	carrier & waste tank	14	electric heater

Fig. 6 - 1 Schematic drawing of an automated trace analysis container

6.2.1 Sample supply tubing

To supply the container with sample, gas, power and telecommunication, a joint connection board was placed in one corner. Every lead-through had a special sealing aperture to avoid that rain or dust enter the measuring container. For waste water applications solvent glued PVC tubings and fittings (G. Fischer, Herzogenburg, Austria) were used for the sample supply and waste connection. The filter was supplied in bypass with sample, therefore an in- and outline were installed. The third grey tubing was needed to pump the waste from the waste collection system into a transport container placed outside the cabin. Details about the tubing and the connection board can be seen in Fig. 6 - 2.

Fig. 6 - 2 Grey PVC tubing for sample supply (bypass) and waste line with connection board

6.2.2 Automated two channel filter unit for waste water

The sample and reagent tubing on the digestion unit ranges from an inner diameter of 0.75 to 1.0 mm. To prevent the blocking of the tubing the largest particle needs to be at least three times smaller than the inner diameter of the supply channels. The sample supply is coming from a waste water bypass feed stream. The solution needs to be homogenized and solid particles should be shreddered to pump them as slurry. Pumps with cutting rotators can do this job, but the particles will still be larger than 0.25 mm. Fats and oils in the sample may additionally lead to coating and deposits inside the sample tubing which further decreases the maximum lead-through opening. To permanently provide the sample to the flow system and to avoid regular disruption a two channel cross-flow filter was installed in the system. The chosen filter units are normally installed in P and N-Analyzers for large municipal waste water plants for similar sampling tasks. The working principle can be seen in Fig. 6 - 3. The sample with large particles flows through the cylindrical filter cartridge allowing only liquid and small particles to penetrate the cylindrical filter sieve. Filter sieves with 100, 150 and 200 µm are available. The advantage of this filter system is the automatic rinsing of the filter surface to free it from bulky materials. High pressure peaks on the collection side can clear the filter pores. In this case the service time of the filter unit between the necessary manual cleaning services is extremely extended.

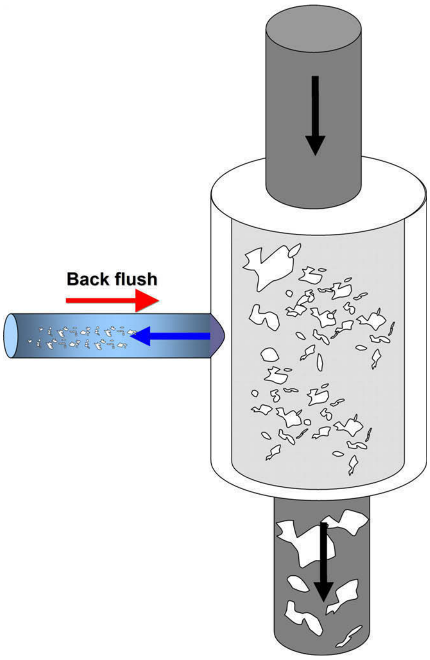


Fig. 6 - 3 Working principle of the cross flow filter

The collection zone behind the sieve is connected to a flow meter and a collection vial. The unit can be programmed to backflush the cylindrical filter cartridge in case of blocked sieves. The amount of sample filtered can be adjusted by setting a certain backpressure in the bypass system which pushes the sample through the filter. Another needle valve on the flow meter unit is used for the fine-tuning of the delivered sample amount. Switching valves between the two channels allows manually maintenance and cleaning without having to stop the filtration. In position 1 filter cartridge 1 will provide sample for the digestion while channel 2 is empty and can be maintained. In position 2 the filtrate is delivered from channel 2 while channel 1 can be serviced (see Fig. 6 - 4).

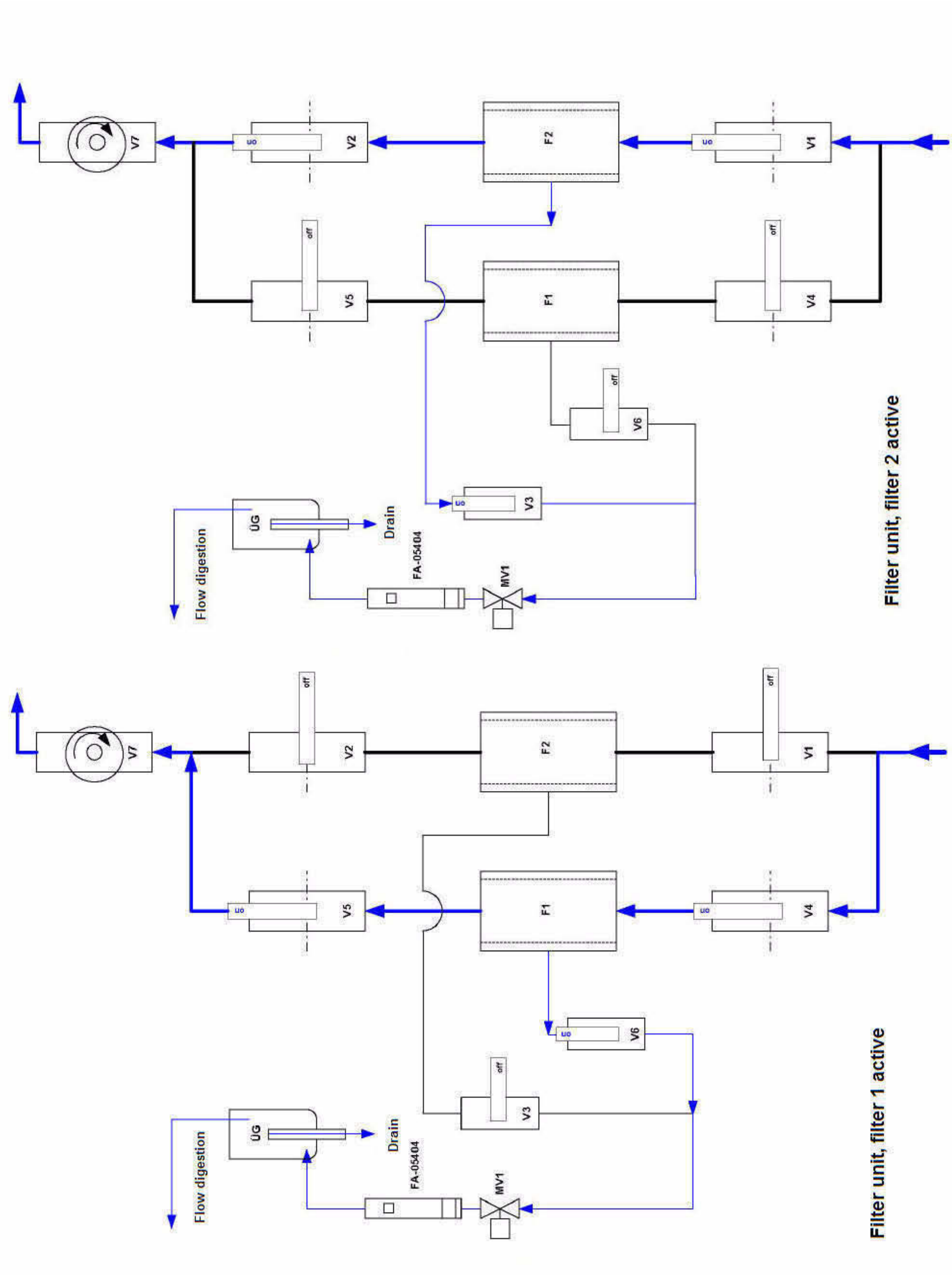


Fig. 6 - 4 Flow chart for the two channel filtration unit

Automatic magnet valves, switched by a build-in controller and a pressure piston, are used to rinse the active filter with a back-flush. The valve heading to the flow meter closes while the pressure piston builds up a short pressure peak with the help of a pressurized air supply. The filtrate in the tubing is used to rinse and purge the filter cartridge from blocking materials in order to extend the service time for manual cleaning of the filters (Fig. 6 - 5).

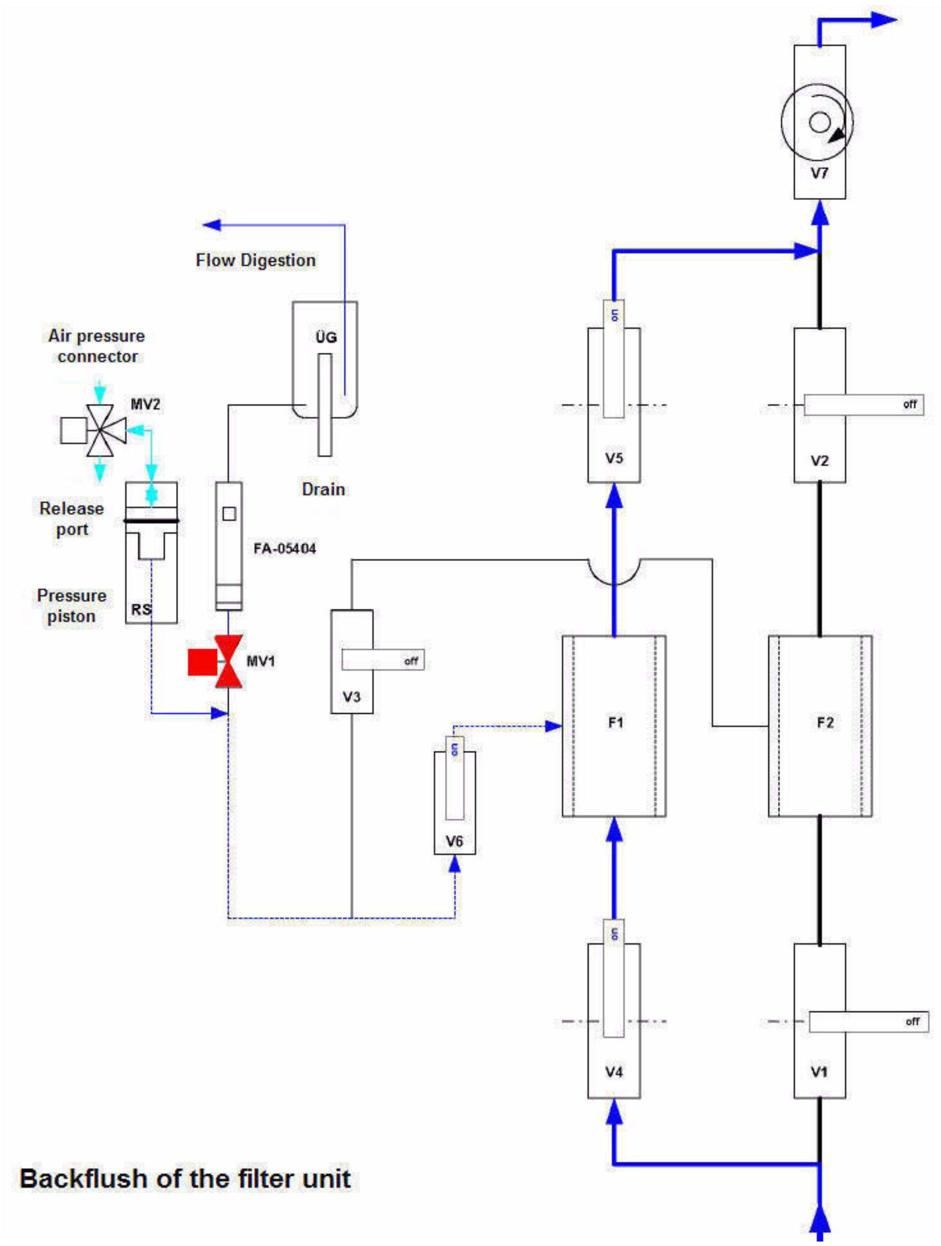


Fig. 6 - 5 Back flush rinsing for the filter for extended service time

The collection container allows to take out solution via a hole in the black cap, a central bleeder limits the amount of sample in the beaker. Another port with a valve in the bottom part is used to take out sample manually or for cleaning of the sample container. The complete filter unit, made of stainless steel components is shown in Fig. 6 - 6.

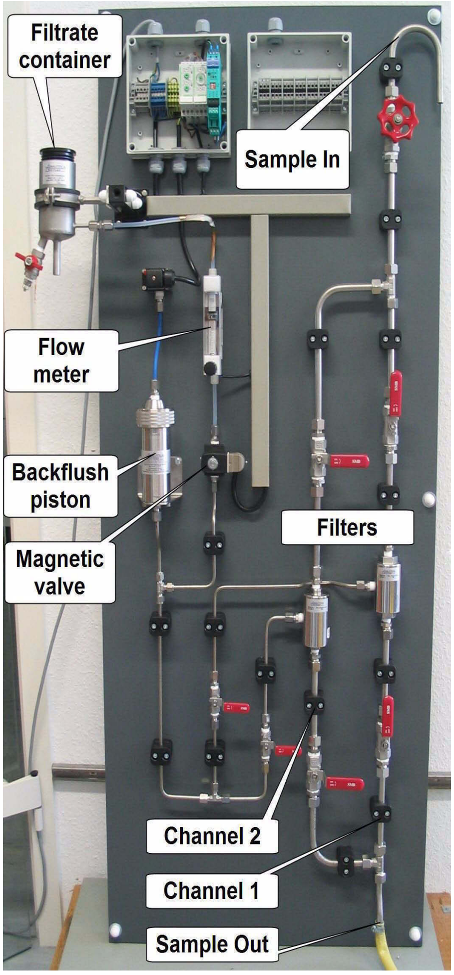


Fig. 6 - 6 Two channel filter unit with flow-meter and back-flush-system

6.2.3 Flow digestion system - Prototype1

The first complete prototype of the flow digestion system was installed on an industrial frame system with extruded aluminium profiles and stainless steel sheet covers allowing simple modifications by simple changes of the steel sheets that work as component carrier. The closed design avoided acid attack of the electronic components which are needed to control the valves and pumps from vapor and spillage in case of broken tubings or leaks. A protection shield in front of the system avoided danger to the operators in the container. An industrial programmable controls was installed to control the high pressure unit, the dosing pumps and the valves. Finally the pressure, temperature and bubble sensor completed the setup used for online digestion. All tubings and fittings for the system were supplied by Upchurch, Oak Harbor, USA.

On the left side the two pump-valve units (Cavro XLP6000, Tecan, San Jose, USA), needed to transfer sample and reagents, are installed (see Fig. 6 - 7). Below them a 4-channel degassing unit (Techlab, Erkerode, Germany) for the carrier solutions can be seen. Each pump is supplied via one channel with diluted acid while the reactor uses two combined channels to prevent gas bubbles from entering the high pressure pump. On the left side of the instrument an emergency switch is installed to stop the instrument in case of a serious error.

Fig. 6 - 7 Flow digestion prototype, left-side view

The two pumps on the left side supplied the two 6-port distribution valves for the sample and acids (Cavro Smart Valve, Tecan, San Jose, USA) which can be seen in Fig. 6 - 8. The connection tubing between the pumps and the valves are made of 1/8’’ PFA tubing with an i.d. of 2 mm. The volume of the tubing’s loops is used as storage and protects the pumps against contamination and acid attack from the sample or concentrated digestion acids that are connected to the valves. In addition to the reagents and acids also air, standard solutions as well as the waste ports are connected to every valve.

One port of each valve is heading to the mixing-T to fill the PEEK-sample loop installed on the injection valve. The high pressure injection valve was a 6-port, 3-channel semi-prep-PEEK valve with a motor drive K6 (both Knauer, Berlin, Germany). The reaction pressure was built up by the same ceramic piston HPLC-pump described earlier. Between the injection valve and the pump a high pressure sensor (Keller, Winterthur, Switzerland) was installed to control the reaction conditions. The cylindrical part in the center contained the titanium tube reactor with glass-wool isolation. In the right-hand corner the air-cooler and the backpressure regulator can be seen.

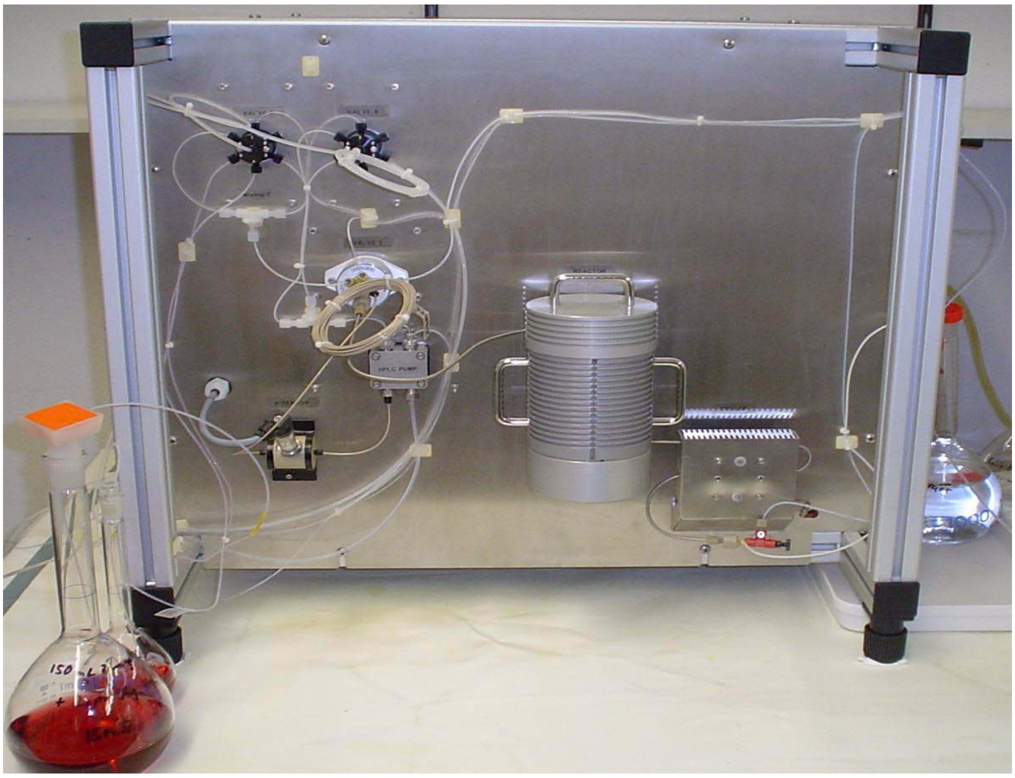


Fig. 6 - 8 Frontal view showing acid/sample mixing and the high pressure components

The right-hand side of the unit was reserved for the collection and distribution system. One valve controlled the collection into the provided vials (see Fig. 6 - 9). There were four vials for samples, one for a QC sample and one for the blank. The caps included a lead-through for sample-in and sample-out as well as a venting tubing connected to a vacuum exhaust system. This tubing was needed to remove noxious reaction gases from the containers. The digestion solutions from the two sample vials as well as the QC and blank were supplied to the connected ICP via the distribution valve. The two other ports supplied the ICP-OES with carrier (diluted nitric acid with 0.5 Mol/L) or with a multi-elemental recalibration solution, respectively.

Both valves are identical to the applied acid and sample valves on the front panel of the system. This feature should allow to keep the number of different spare parts low. An optical bubble sensor was used to determine air in the tubing which indicated empty vials after purging their content.

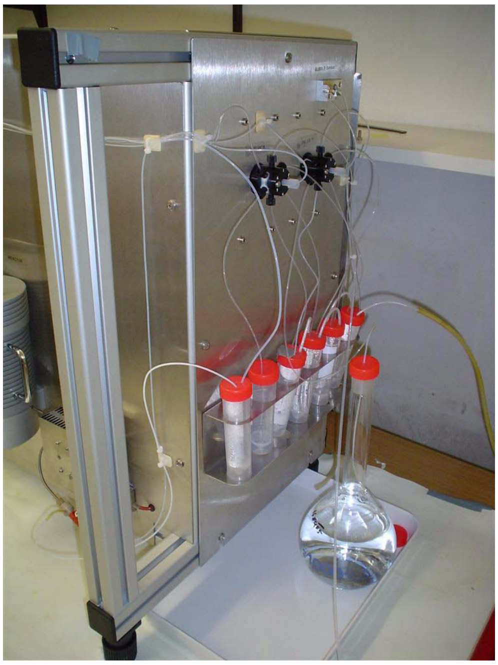


Fig. 6 - 9 Sample collection and distribution valves with collection vials

6.2.4 ICP-OES Optima 4300 DV from PerkinElmer

The installation in the test container used an ICP-OES Optima 4300 with dual view system for the online monitoring of the waste water samples. The instrument was installed on a heavy-duty trolly to allow easy service and maintenance. The software version for analysis and system control was WinLab 3.1.

6.2.5 Control-PC for monitoring, digestion and measurement software

A Windows XP based PC was used to monitor the container including filtration, gas supply, digestion and measurement. The synchronization between the ICP-OES and the digestion system was done via a software interface between the flow digestion control software and WinLab 3.1 on the PC. After the flow digestion system announced a finished digestion, the synchronization software started the measurement. The solution was supplied via the distribution valve to the ICP-OES. Meanwhile, the next sample was processed in one of the empty sample vials. After finishing the last replicate measurements the vials were emptied by the peristaltic pump of the ICP-OES. As soon as the bubble sensor detected air, the system was ready to use the empty vial again. The small residual droplets in the container did not influence the results significantly as the goal was to determine a monitoring in which uncertainties of 10-15 % are not critical. In addition all container filling levels (acid, carrier, waste, argon) and also possible errors like leaks could be monitored via the corresponding ports on the industrial controller. With remote desktop control it was possible to check, restart or stop the process.

6.2.6 Argon supply system

The container was applied with an argon supply system which allowed the connection of two bottles, each 50 L at 200 bar, inside the container for 24 hours of uninterrupted operation. When installing two bundles with twelve bottles each it was possible to run the ICP-OES without changing the bundles for more than one week before the gas containers needed to be changed. A combined pressure regulation and switching unit between the two bottle connectors provided automated delivery from the container with lower pressure until the filling pressure was similar to the regulated supply pressure. A digital pressure sensor box monitored the pressure in the two connection ports. By connecting the alarm ports of the sensor box to the controller unit of the flow digestion system online filling level monitoring was available.

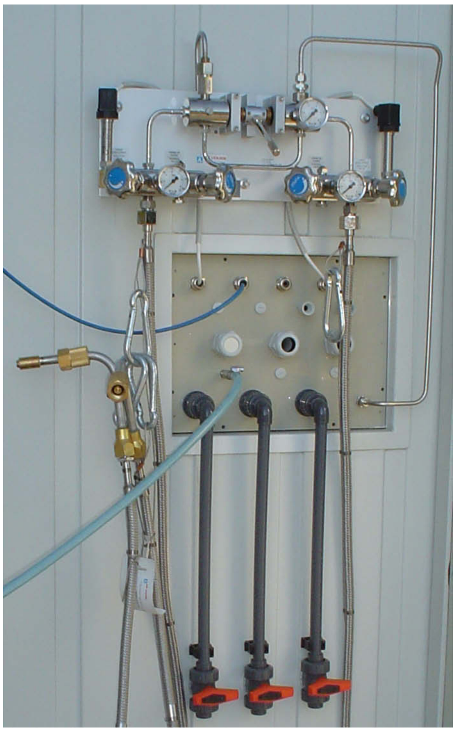


Fig. 6 - 10 Argon supply system for two bottles or bundles

6.2.7 Carrier and waste tank

The flow reactor needed 3.6 L carrier for one day of operation. Before and after every sample and for the ICP-OES rinsing additional 4 L of diluted acid were needed. The carrier tank with 65 L contained a nitric acid solution with 40 mL concentrated HNO_3 / L (~ 0.4 M) and was big enough for more than one week of operation without interruption. The waste tank also had 65 L to collect the used carrier as well as acids and samples which are added to the carrier during the process. The carrier tank was monitored at the bottom (approximately at the 15 L level) with an inductive level sensor mounted outside the container. The same sensor (microBOX, SIE-Sensorik, Viernheim, Germany) was connected at the top of the waste tank to stop the process in case of overfilling (Fig. 6 - 11),

As electronic sensors are not valid for safety switches two additional mechanical floating level switches were installed in series in an additional collection tray beneath the containers and the filter unit. In case any reagent or sample is spilled the system shutoff completely, stops the waste water pump and the digestion system.

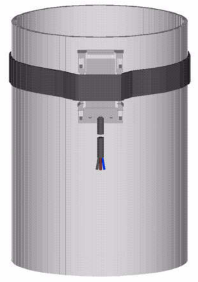


Fig. 6 - 11 Inductive filling level sensor fixed outside of the containers

6.2.8 Compressor, air drying and air filter unit

In the left-hand corner a place was reserved for the installation of a compressor unit supplying the ICP-OES and the filter unit with pressurized air. Due to the existing pressurized air supply on the test installation site instead of the compressor only an air-drying and filtration unit (Jun-Air, Ahrensberg, Germany) was installed to provide high quality air for the ICP-OES.

6.2.9 Container exhaust system

For the operation of the ICP-OES and the digestion system a strong exhaust system was needed to remove noxious gases. Due to the small size of the container and the large volume of argon, which emerges when a bundle of 12 bottles with 50 L each is used, the function of the exhaust system needed to be monitored. Two independent differential pressure switches, installed inside the exhaust tubing cross-checked the proper function of the exhaust unit. Only a working venting system allowed to open the magnetic valves of the argon supply system. Two valves in series were needed to guarantee failproof operation of this essential safety system. The exhaust system was made of acid resistant components and had a flow rate of minimum 400 m³/h and was installed by the container supplier (Tritec, Pettenbach, Austria).

6.2.10 Air condition system

The isolation of the container with glass wool had a thickness of 8 cm, the normal heat uptake through such a wall on hot summer days should be below 2 kW. Due to the operation of a high power ICP-OES with the sensor cooling unit and a strong air exchange by the exhaust system the needed cooling power was estimated at 6.5 to 7 kW. As a 10 kW freecooling system was only slightly more expensive than a 7.5 kW system the freecoling system was installed to have reserve in case of unconsidered higher heat inside the container. The freecooling device allowed to apply fresh air from outside through a filter system in case the external temperature should be below the inner temperature. The advantage is that in such a case the compressor could be deactivated which saves running and service costs due to shorter operation times. Depending on the dust load the filter in the air condition system needed to be cleaned at least twice a year to keep the air exchange rates within the limits. The operation range in summer was 28 to 30 ℃ to limit the thermal difference between the out- and inside of the container. During winter time the heat produced by the ICP-OES itself and the ICP-OES cooler was enough to keep the temperature above 20 ℃ due to the good isolation of the container.

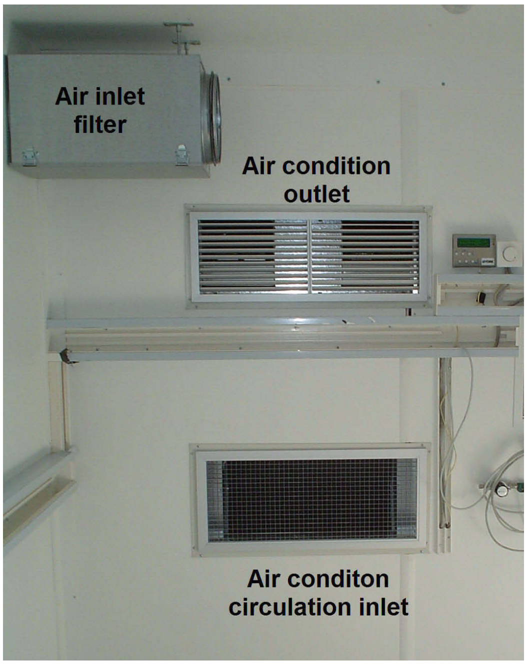


Fig. 6 - 12 Air condition ports for free cooling and circulation and the additional air inlet filter respectively

6.2.11 Waste and drain

The filter unit took in adjustable amounts of sample via diversion from the waste water feed stream, but they were in all cases much higher than the amount needed for the flow digestion. The excessive amounts of sample were automatically drained back to the waste feed stream via a waste and drain system. Due to the flow rates of typically 30 to max. 150 mL per minute from the filter it was not possible to store the waste material within the waste barrels inside of the container.

6.2.12 Air inlet filter

The continuously running exhaust system maximally extracted 400 m^3/h from the container. In case of cold temperatures outside the air condition system supplied the container with fresh air via the build in filter system (see Fig. 6 - 12). For the operation at hot temperatures or extreme cold conditions with a closed air inlet latch an additional filter box allowed to vent the container with fresh air. The box was equipped with an exchangeable class F7 filter cartridge to avoid dust contamination inside the container.

6.2.13 Switch box

The electric switch box next to the standard power line protection also switches the safety control unit for the exhaust system monitor. By means of this unit it was possible to deactivate the argon supply. Without enough pressure the ICP-OES and as a consequence the flow digestion system stopped operation.

6.2.14 Electric heater

In case of too low environmental temperatures or during an interruption of operation in winter the electric heater was needed to keep the inside temperature above freezing point. With the help of a build-in freeze protection the temperature was kept at 5°C (see number 14 in Fig. 6 - 1).

6.3 Installation and setup

6.3.1 Test sites

Two available test sites were evaluated for the investigation of the prototype container; a large printed circuit board manufacturer and a metal coating factory, both situated near Graz, Austria.

The waste water of the printed circuit board (PCB) producer mainly contained copper and iron salts as well as relatively low concentrations of mineral acids and detergents. Due to the wide range of different coatings the waste water of the second site contained a variety of heavy metals. The installation near the water treatment facility opened the possibility to check both, the raw waste water and the cleaned drain. The analysis of the two streams was useful to control the efficiency of the cleaning process.

Because of the higher organic load, the higher number of heavy metals to analyze and the proximity to the Anton Paar headquarter the metal coating company was chosen as test site for the prototype container.

At the site the process waste water, coming from the different baths, is first treated with a neutralization and precipitation bath, followed by a filtration and an ion exchange treatment to remove toxic elements. Depending on the nitrite concentration an optional denitrification line is available to reduce the concentration below the according maximum levels of governmental regulations. The treated and purified water (approximately 60 m^3 / day) is drained to the local municipal waste water plant.

For the routine operation of the plant permanent monitoring is not necessary although some single parameters like the phosphate and nitrite concentrations have to be checked twice a day. The heavy metal concentrations are controlled only 4 times a year during routine monitoring checks.

6.3.2 Transport and installation

Before the complete system could be transported it was necessary to remove the instruments as well as the installed tables for the ICP-OES, the flow digestion system, the control PC and the workbench. The gas supply, exhaust unit, air-condition and filter were permanently installed. The weight of the empty container was approximately 3.0 tons and therefore low enough to be lifted with the help of a truck lift which was installed on the transporting truck itself (see Fig. 6 - 13).

Fig. 6 - 13 Container transport with a truck with heavy load lift

The container and the gas bundles were installed in front of the waste treatment location in the basement of a factory building. Together with the waste in- and outlet a pressurized air tubing as well as an electric power supply and network connection cable completed the needed infrastructure. The container was installed from July until November to cover both, extreme hot conditions to see the efficiency of the air condition system as well as lower temperatures to determine problems with condensation or freezing liquids.

Fig. 6 - 14 Container with argon gas bundles in front of the waste water treatment building

Instrumentation, waste containers, work benches and accessories were reinstalled after installation of the container and connecting the supply lines. In Fig. 6 - 15 two different views of the completed container with the flow digestion system, the ICP-OES and all the needed infrastructure can be seen.

Fig. 6 - 15 Completely installed container ready for continuous operation

6.3.3 Configuration

After completing the installation the entire facility needed to be configured and started up. In addition to the filter and the supply pump settings the digestion method and the ICP-OES parameters needed to be optimized. Data and instrument monitoring was installed on the PC which was accessible from any other computer connected to the internet via a firewall. The most critical part of the system start was the synchronization between the flow digestion- and the ICP-OES-software.

Digestion system configuration:

The following digestion method was developed offline with test samples from the neutralization bath before the installation.

Flow rate:	2.5 mL/min
Sample & reagent volume:	max. 5 mL sample and 2.5 mL reagents
Reaction conditions:	10 mL reactor coil; 4 min at 300℃ and 150 bar +/- 30 bar
Collection volume:	20 - 30 mL

The sample valve was configured to take solution from the filter unit and from a flask containing a QC sample with the elements in quest. The acid valve took solutions from two different acid containers 1:1 diluted HNO_3 and concentrated HCl as well as a Sc solution which was used to check the completeness of the collection. Two collection vials were reserved for samples. One vial was intended to collect the QC sample and another for the blank digestion.

Pump and filter unit configuration:

A metal free pneumatic membrane pump was used to transfer the sample slurry from the neutralization bath from the basement of the factory to the container. The pump was made of a PP casing with a Santopren/PTFE working membrane and PTFE ball valves as check valves. The robust design allowed a maximum particle size of 2 mm in the pumped liquid. The maximum pump rate was up to 56 L/min when supplied with maximum air pressure. Normally the amount was limited to less than 10 L/min because this was more than enough for the analytical task. The suction height was 1.5 m and the delivery head 2.5 m. A plastic sieve with a mesh size of 1.5 mm on the suction hose avoided pump blocking by large particles. To prevent environmental pollution in case of a hose breakage the forward and backward lines were protected with an additional supporting hose containing the sample hose, a waste hose as well as the power and pressure supply lines.
The filter unit was equipped with two 100 µm filter cartridges.The flow from the filter to the sampling cup was set to 2 L /min.

ICP-OES Configuration:

The used ICP-OES was installed with a standard Ryton Scott spray chamber and a crossflow nebulizer. The Al_2O_3 injection tube and the torch were original PerkinElmer standard components. For the online operation the delivered WinLab software, which was installed on the control PC, was used to operate the instrument by using the internal processes of the software. For the application of sample lists one autosampler was activated in the configuration and operated in simulation mode. This settings were necessary to use the standard software together with the synchronization software FDS-Bridge. Due to the limited number of free ports on the distribution valve only a two point calibration with blank and high concentration standard could be used. The other ports were needed for the two sample vials, the blank and the QC sample digestion respectively. For further configurations at least a four point calibration was requested to increase the precision of measurement.

FDS-Bridge software configuration:

In addition to the control software for the flow digestion system another software was developed to synchronize the ICP-OES-software WinLab with the online digestion system and to react on alarms and system warnings. As it has a bridging function between the flow digestion system and the ICP-OES, it was named FDS-Bridge. Different tasks like the plasma ignition, loading of the sample list or the methods are organized in WinLab by internal routines. The new synchronization software started the different subroutines like a normal user would do when clicking on the WinLab icons. The needed parameters, like new sample lists, were entered automatically. Clicks on buttons like the run and hold buttons of the autosampler routine were simulated too.

The autosampler was activated in the software and operated in simulation mode to be able to use sample lists. This allowed to start a predefined list of samples, blanks and QC's with only one standard list loaded every day after midnight. FDS-Bridge only needed to start the list, pause after every injection and continue once the sample was totally finished by the digestion system. The list also contained the samples, the positions of blanks and the QC samples. The predefined sample type (unknown sample, blank or QC) in the process list controlled the ports of the digestion system. In case of alarms like missing reagents, overfilled containers or empty gas bottles the software immediately stopped the operation of the system. The sample list contained the maximum number of samples applicable per day. In case of normal operation the system followed the list until midnight before a new list was set in operation.

6.3.4 System startup

Using desktop remote features it was possible to manipulate many different parts of the system, but there were still some components which needed manual activation or settings. Automation of these points would have cost too much effort or would have been useless as they are combined with other manual actions like changing gas bottles or mixing new standards.

Manual startup actions:

The following manual steps were necessary to start the system:

- Activation of the venting system and the air condition system
- Activation of the ICP-OES cooling unit
- Opening the manual gas tank valve
- Opening the shear gas supply line
- Power on the ICP-OES, mount the pump tubings and adjust the clamps
- Power on the flow digestion system
- Starting the PC and automated start of WinLab, Automation Studio and the FDS-Bridge
- Preparation of the carrier, reagent and standard solutions

Automated startup actions:
Once the mentioned steps are performed the system can be operated by remote desktop from a PC via the control board and the relays installed in the flow digestion system. After purging and stabilizing the ICP-OES spectrometer thermally it was possible to ignite the plasma. Parallel to the ICP-OES start-routines the flow digestion system was started. The detailed starting routine is shown in Table 6.1.

Table 6.1: Automated system start-up routines

Step	Action	Note
Purging connection tubes	the 2 pumps fill all tubings connected to the sample and the acid valve	remove air and old reagents in the system
Rinsing sample/acid loops	rinsing of the sample/acid loops with carrier after filling the connection tubing	avoiding cross contamination
Filling injection loop	both pumps take up carrier and fill the injection loop	removing air from the loop
Priming the reactor	the high pressure pump fills the reactor with carrier at a low pump rate	priming stops at 20 bar; time-out in case of a leak
Preheating the reactor liner	Heating the filled liner to 200 ℃ to soften the liner	
Liner shaping	the high pressure pump increases the pressure to 100 bar with low flow rate	the PTFE-TFM liner expands to fill the gap between the liner and the Titan tube
Heating to digestion temperature	temperature increases to the adjusted 300℃	the high pressure pump maintains the pressure running with low pump rate

Finally it was necessary to start the pneumatic slurry pump to supply the filter with sample solution. The first time it was necessary to adjust the amount of sample manually, passing the filter and flow meter with an adjustment needle valve. After all these steps the system was ready to start with the automated sample preparation and measurement.

The flow rate during the final heating step was set to 0.25 to 0.50 mL/min to avoid losing too much carrier and energy due to the cooling effect. The pressure during this heating phase must constantly remain at minimum 100 bar to avoid boiling inside the system. The pressure was set manually to approximately 120 bar at standby pump rate with the help of the backpressure valve. This value increased to approximately 150 bar at the working flow rate of 2.5 mL/min. The pressure setting and adjustment were done manually before the first start and had to be repeated maximum weekly because the pressure value did not change more than maximum 5 to 10 bar per week.

6.3.5 Digestion and measurement

The FDS-Bridge software loaded a new sample list containing regularly QC and blank samples during every program start. This checks were done after 5 to 10 real samples. The list also included commands for regular ICP-OES-calibrations and recalibrations. Every sample list started with a blank and standard measurement to calibrate the ICP-OES. The needed solutions were supplied via the distribution valve of the flow digestion system.

Calibration and sample mixing

The ICP-OES calibration started parallel with the preparation steps for the first sample digestion. The needed steps for the sample preparation are explained in chapter 5.2. It took approximately three minutes for the rinsing and mixing procedure. After injection another 2 minutes waiting time was needed before starting the sample collection in vial number one. Depending on the final dilution to 15 or 25 mL the sample collection took 6 to 10 minutes. The formed reaction gases mixed the collected solution as the collection tube pointed to the bottom of the conical sample vial. This setup provided a homogeneous sample solution for the following measurement using the ICP-OES.

Measurement

As soon as the flow digestion system had finished the collection the distribution valve switched to the corresponding port to provide the digestion solution to the ICP-OES. The FDS-Bridge started the ICP-OES measurement at the same time with minimum 2 minutes rinsing time to get rid of the remaining solution in the tubing from the previous measurement. After the defined number of replicated measurements the pump switched to flash mode to empty the collection vial faster into the waste container. Three seconds after the bubble sensor had detected air in the connection tubing to the ICP-OES the first sample was finished. The FDS-Bridge paused the ICP-OES measurement sequence until the next sample was collected and ready for measurement. The finally empty vial was reserved for the next but one sample.

Time saving due to parallelized actions

While the first sample was measured the next sample was already collected in vial number two. The sample uptake and mixing with reagents had already started during the end of the collection phase of the first sample. As soon as the previous collection was finished the next sample was injected. The FDS-Bridge typically had to synchronize two to three processes at the same time: mixing of the sample and reagents, collection of the samples and the measurement via the ICP-OES.

Regular QC and blank checks

Depending on the sample list the system run blank digestions or QC samples. The QC procedure differed to normal samples only regarding the used port on the sample valve. The blank digestion on the other hand only filled the injection loop with the internal standard and reagents. The collection and measurement was equal to normal samples despite the different ports and vials. Separate containers were used to avoid possible contaminations of the real samples. Finally the system also had to run recalibrations with the high concentrated standard and the carrier as blank respectively.

Log and sample files

The FDS-Bridge logged all sampling, recalibration and measurement times. The software also interrupted the measurement and digestion shortly before midnight to load a new sample list. Early in the morning the process started again with a new list and new samples.

High throughput

The throughput for the mentioned operation was around 80 to 120 samples/day depending on the number of QC- and blank-samples, the recalibrations and the collection volume. The time limiting factor of the complete process was the collection time of the samples, all other tasks ran parallel and did not take as long.

6.3.6 Regular maintenance

The goal of the test installation was to run the container without the presence of an operator. Two control visits from the waste water plant personnel per day should be enough in addition to the weekly maintenance visits by a skilled operator. The containers for the standards, reagents and the waste as well as the gas supply were big enough to ensure 7 days 24 hours operation.

Weekly Maintenance:

During the weekly inspection the following maintenance and service tasks should be done:

a) filling up the reagent containers with new digestion acids
b) emptying the waste container: the content could be drained into the collection and neutralization bath
c) preparation of new QC- and calibration standards
d) replacement of the empty argon bundle by a new one
e) inspection of the amount of collected drain liquid from the reactor used as reactor condition indication
f) replacement of the ICP-OES peristaltic pump tubing
g) switching the filter channels and cleaning the used filter cartridge if needed
h) rinsing the sampling cup and the flow meter

The different steps could be done without interruption apart from the few minutes the ICP-OES pump needed to be paused for the pump tubing exchange

Quarterly Maintenance:

Due to the large number of samples per day and the relatively high salt load in the raw solution the setup needed an intensive maintenance every three months. In add to the weekly routine tasks it was necessary to clean:

a) the ICP-OES spray chamber, injector and the torch
b) the filters of the air condition, inlet filter box and all ICP-OES cooling fans
c) the high pressure injection valve

On the flow digestion system the reactor as well as the sample loop and connection hose between the sample filter unit and the digestion system had to be changed. Together with the reactor a refurbished backpressure regulator was installed to replace the used one. The elastomer membrane adjusting the pressure became hard due to mechanical and chemical stress. This hardening caused high pressure jumps when switching from standby to operation flow rates. Replacing the standard material Viton with a PFA coated Kalrez membrane improved the chemical stability and longtime flexibility. After a restart the system should be ready for the next 3 months of operation.

6.4 Performance and service time

6.4.1 Test program

The goal of the 5-month-test-period was to determine the strengths and weaknesses of the setup. In addition to the analytical performance the reliability of the hard- and software should be verified. The operation at realistic conditions should help to improve the setup of the container and its installed components. During the test phase the container was not only visited twice a day from the local personnel, the analytical station was also monitored with the help of the installed PC remote features.

6.4.2 Reactor service time

The reactor used in the container for the test period was made of titanium tubes with 2.2 mm i.d. and PTFE-TFM liners with an o.d. of 1.6 mm and an i.d. of 0.75 mm. The liners therefore needed quite a remarkable expansion to get shaped to the supporting tube. As described before (chapter 4.10.1) this liner was extremely stretched after applying the working pressure leading to a short lifetime. Therefore later on a liner with a larger diameter was used (chapter 4.10.3).

Table 6.2: Service life time for the lined reactors during the container tests

Reactor	Installed	Replaced	Time [h]	Comments
1	12/11/04	20/01/05	**140**	Overheating > 350 °C due to a temperature regulation error
2	24/01/05	07/03/05	**423**	Reactor damaged due to repeated high pressure pump failures: liner permanently overstretched
3	12/03/05	16/04/05	**642**	Strong increase of diffusion, corrosion of the titanium tubing
4	16/04/05	16/06/05	**1563**	Replacement of the reactor as the diffusion rate exceeded 25 mL/day
5	20/06/05	08/08/05	**830**	Reactor damaged due to repeated high pressure pump stops during software tests: liner permanently overstretched
6	08/08/05	12/09/05	**718**	Replacement due to pressure drops, but the failure was caused by the high pressure valve
7	14/09/05	07/11/05	**804**	Reactor damaged due to repeated high pressure failures due to injected air caused by the sample filtration unit
8	23/11/05	19/12/05	**472**	Reactor blocked several times due to too high slurry amounts causing too many restarts; heating cartridge failed

6.4.3 Continuous online measurement of a waste water feed stream

The following diagrams show some results measured during the test period for the reactor 6. The measurement started after a service action at noon and continued until midnight. There the process stopped automatically and reloaded a new sample list for the next day. During this test period the system recalibrated after every 10th sample using a blank solution and a high concentrated standard for a two point recalibration.

ICP-OES measurement conditions for the Perkin Elmer Optima 4300 DV:

- PerkinElmer cross-flow nebulizer with a Rayton Scott double pass spray chamber
- HF-Power: 1400 W
- Gas flow settings: nebulizer: 0.8 L/min; auxiliary: 0.2 L/min; plasma: 15 L/min
- Pump rate: 1.2 mL/min
- Axial view

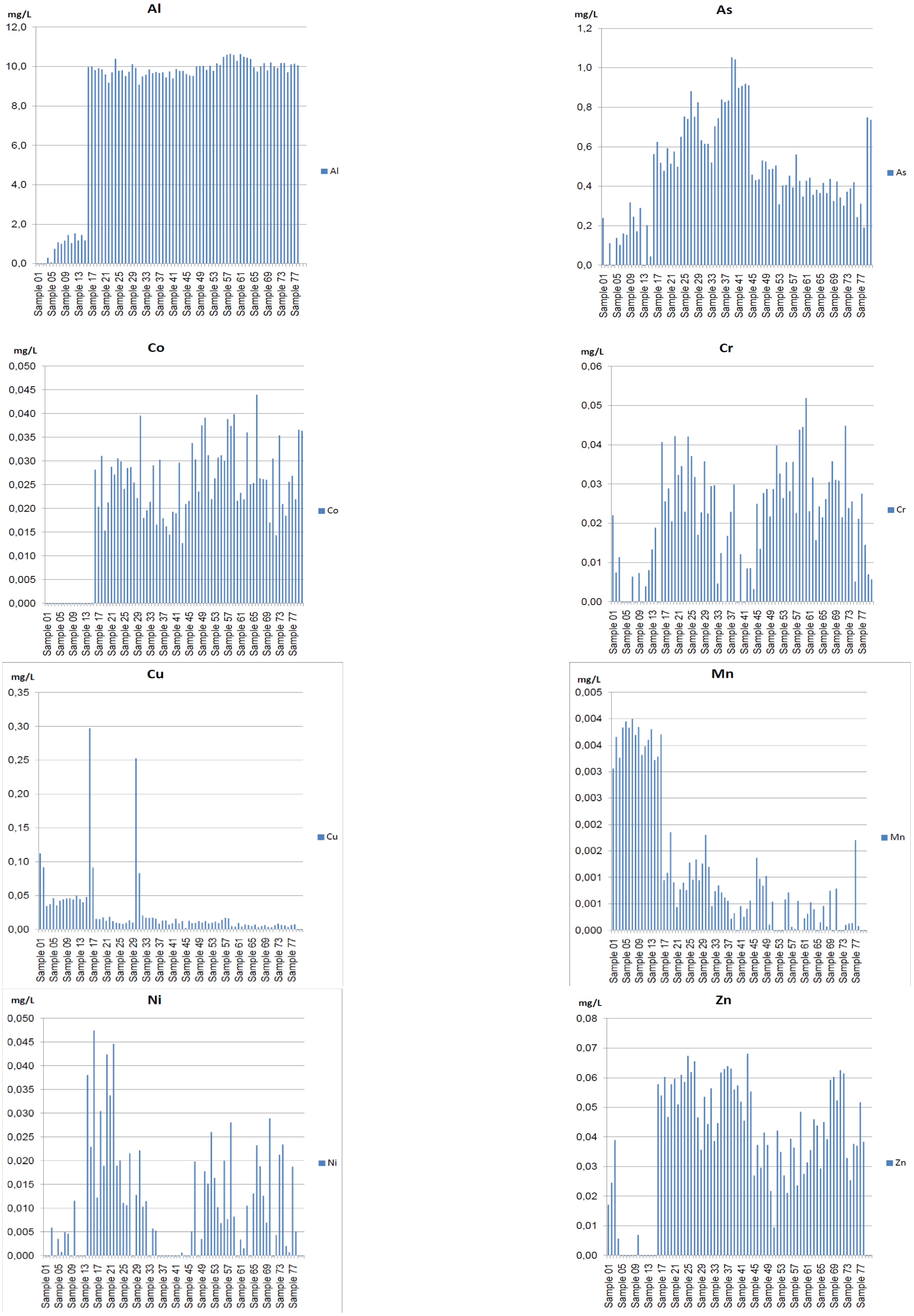


Fig. 6 - 16 Determination of 8 elements in waste water using online digestion

6.4.4 ICP-OES measurement

During the intensive testing period in August 906 samples were measured. Due to vacation and service needs in September and October only 936 samples could be measured. There were only a few days with more than 90 samples/day, on all other days problems with the bubble sensor or valve errors caused interruptions. In some cases only maximum 50 samples or less could be processed. The ICP-OES itself worked without troubles during the operation period. The weekly installation of new pump hoses and the cleaning of the spray chamber and the injection tube every 3 to 4 weeks were sufficient to operate the system continuously without failure.

6.5 Troubleshooting

In the last chapter the system's performance, the number of digestions and the service time of the components were discussed. The reason for the numerous interruptions and errors were analyzed for further optimization processes.

Main difficulties at the beginning were caused by the filter unit. The issues started with a permanently blocked flow meter and continued with leaks and corrosion of the connection fittings. Another constant problem was the optical bubble sensor indicating empty vials. Wrong readings stopped the process, sometimes several times a day needing a manual restart or readjustment. After 6 weeks of operation another malfunction appeared for the first time: leaks from the 6 port distribution valves. Detailed information about the difficulties, counteractions and solutions are described in the following sections. Due to the high complexity and minor success of some improvements it was only possible to run one week without interruption. During the rest of the testing phase several restarts and manual adjustments between the planned service intervals were needed.

6.5.1 Filter problems

For neutralization of the waste water NaOH pellets and calcium carbonate were used. The formed hydroxide took the majority of toxic elements from solution by coprecipitation. Simple filtration drastically reduced the amount of contaminants. To test the stability of the system for water containing particles the sample was taken from this bath. As only little sample amounts were needed, the flow control meter was set to values of few mL/min.

This low speed of flow and the reduced diameter were the reason for continuing problems: the flaky particles could be pumped, but the separate particles assembled in the flow meter formed plugs which stopped the sample stream. This phenomenon started several hours after the start and caused an empty sample beaker within a short time. Higher flow rates reduced the clogging effects a little, but resulted in another problem. The overflow of the filtrate container was not closed pressure tightly and from time to time the sample spilled out of the beaker. In both cases the system stopped automatically: without sample the system pumped air into the system stopping the reactor due to a longtime pressure decrease. The spilled sample switched a level switch in a waste collection tray beneath the filter. When activated the FDS-Bridge stopped the process and again manual interaction was necessary.

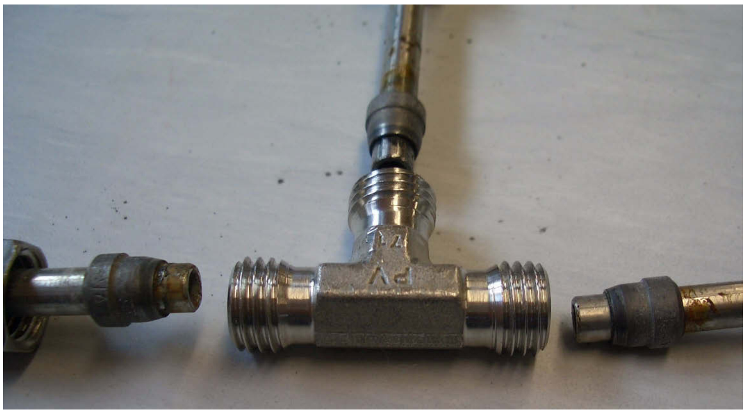


Fig. 6 - 17 Corroded filter unit fittings as source of leakage

Leakages and corrosion of the filter tubings were caused by wrong combination of ferrules and fittings from two different vendors. After replacing and resealing the filter unit, the leakage problem was solved. To avoid clogging of the sample slurry, a 50 µm filter replaced the 100 µm unit, which drastically reduced the amount of particles. The filtrate still contained large amounts of solid particles (2 - 5 % dry matter), but the permanent clogging could be avoided from further on.

6.5.2 Bubble sensor error

The connection between the flow digestion system and the ICP-OES consisted of a PFA tubing with 1.6 mm o.d. and 0.75 mm i.d. and a length of 80 cm. The small inner diameter helped to reduce the dead volume in the connection line, but made the detection of air bubbles difficult. Capacitive sensors are commonly used for such tasks but need larger diameters. The idea to use a short piece of tubing with a larger diameter was rejected due to the risk of carry-over effects in the joints. An optical sensor which is applicable for such small diameters was developed for another application at Anton Paar. The sensor worked with optical refraction, but small droplets regularly caused malfunctions. The small droplets appeared more frequently after a waste pump had been installed (see below). As explained in chapter 5.3.3 an air-filled tubing could give a wrong liquid signal. The FDS-Bridge did not detect the empty vial in such a case and stopped the run. During further development the system included a time-out function which automatically switched the distribution valve to the carrier port. At the same time the waste pump stopped and carrier was pumped via the slow ICP-OES pump. After switching back to the empty sample vial the sensor correctly detected air and released the vial for further samples. In case of a pump error the sensor once again only detected liquid and irrevocably stopped the process.

6.5.3 Plasma overload

At the end of each measuring sequence the FDS-Bridge increased the pump rate of the peristaltic pump to empty the vials faster. In addition to a higher wear of the tubing another problem occurred: the increased flow rate transported too much sample into the plasma. This overload sometimes terminated the plasma and caused faster salt precipitations on the injector. Reducing the pump rate helped to avoid the negative effects, but the time needed to empty the vial was too long. An additional membrane pump and the same t-shaped fitting known for the mixing of reagents solved this problem. As soon as the ICP-OES had finished the measurement the small pump started and removed the remaining sample. The solution was pumped in the connection line with high pump rate via the t-shaped fitting (see Fig. 6 - 18). The check valve was necessary to avoid that waste was pumped to the ICP together with sample. At the end of the suction phase the fast pump rate of the membrane produced the small remaining droplets which were mentioned in the section before. It was not possible to have a plug flow which keeps the liquid together at such high flow rates. The automated stop of the waste pump and a short-time transport of carrier as described above solved the problem with wrong sensor readings caused by droplets.

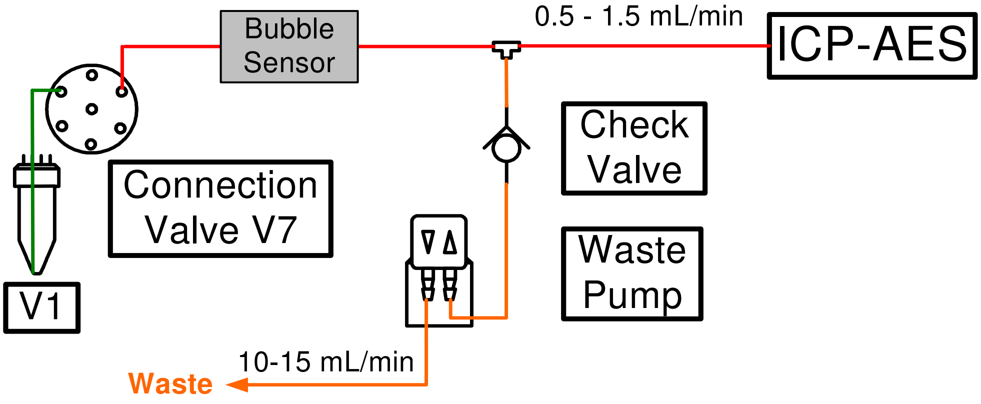


Fig. 6 - 18 Additional waste pump and check valve

6.5.4 Leaking valves and pumps

The most serious problem was caused by the four low pressure distribution valves (SmartValve, Tecan, San Diego, USA). Depending on the pumped reagents the service time varied between 6 weeks for the sample valve and maximum 10 weeks for the distribution valve. The particles in the sample slurry and the high number of switching actions caused the fast abrasion of the sample valve. The damaged rotating PTFE seal released sample solution into the driving electronics (see Fig. 6 - 19).

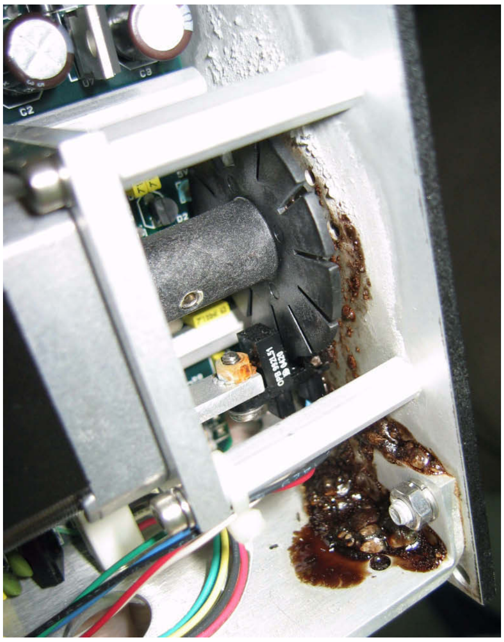


Fig. 6 - 19 Corrosion of the driving electronics for the sample valve

In addition the spring holder which was used to push the conical PTFE rotor into the stator was also chemically attacked. Due to the broken holder the valve released even more reagents, but it continued to work as the drive motor centered the rotor and therefore the entire system continued to work. The other valves had no abrasive particles to handle, but the diffusion of HNO_3 through the PTFE rotor attacked the spring holder made of POM. The result was a leakage similar to the sample valve with chemical attack of the drive electronics. The leaks were detected only after the completely corroded valve drive had stopped operation due to electronic failure. The first measure was to replace the POM parts with holders made of ETFE (see Fig. 6 - 20).

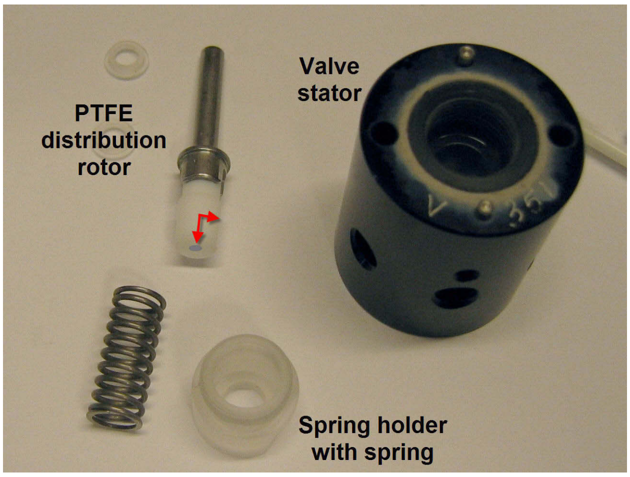


Fig. 6 - 20 Smart valve components with new spring holder made of ETFE

The problem with abrasion of the PTFE seal could not be solved by a different material, only by a maintenance procedure during which the seals were replaced every 4 weeks in the sample valve and every 8 weeks in the other valve units. Two of the three damaged electronic drives could be repaired. The drive shown in Fig. 6 - 19 was too corroded to repair it for further use.

The high pressure valve also needed service during the test phase. After 3 months the particles in the sample slurry caused groovings on the rotor between the channels of the 6 port / 3 channel valve. In this case the effect was less critical for the hardware. The leakage was drained by the waste port of the valve. The first time it was possible to solve the problem by using grade 1000 sand paper to polish the disc (Fig. 6 - 21), for the second time it was necessary to replace the rotor disc. The stator made of PEEK had changed the color but did not show groovings after the test period of 6 months.

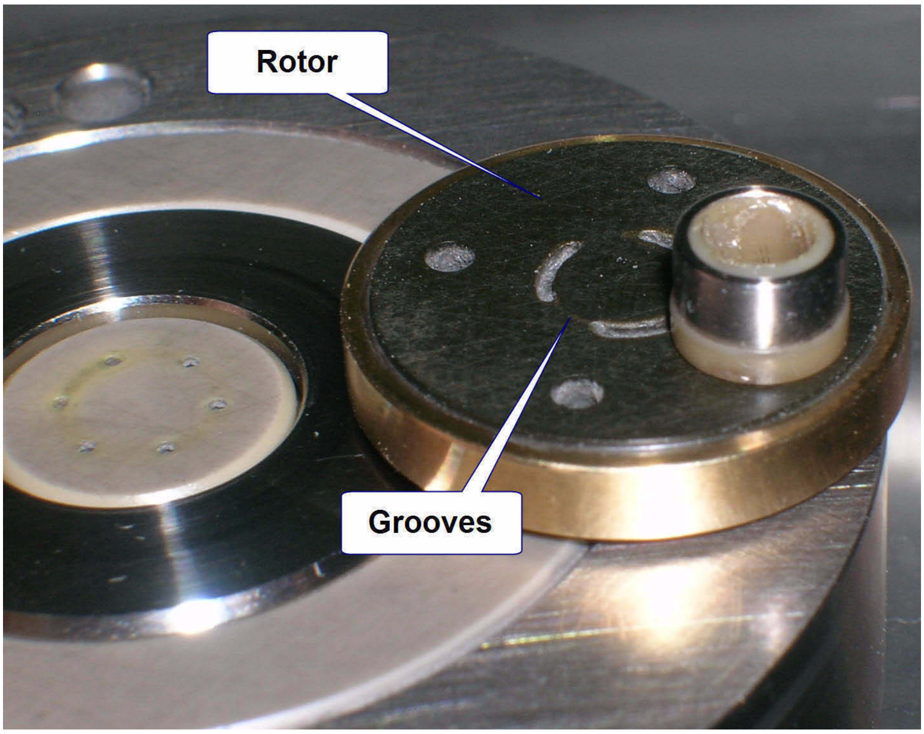


Fig. 6 - 21 Faultless PEEK stator and grooved rotor disk of the high pressure valve

At the end of the test period the ambient temperature decreased to 5℃ during the night. Due to a digestion process failure over night the ICP stopped the operation and the container cooled down to ambient temperature. The restart at the next day failed because the two pistons of the syringe pump modules had shrunk due to the low temperatures. That is why the pumps had taken up air instead of carrier which stopped the restart of the process. After increasing the temperature setting for the electric heating unit from 5℃ to 18℃ and warming the container's content the system could be started again without errors.

6.5.5 Bubble sensor error

The optical bubble sensor, designed to be used for non-polar liquids in density and viscosity instruments caused permanent system stops due to wrong readings. This effect became more critical after using the tubing through the sensor for three to four weeks. Small remaining particles and contaminations on the tubings inner wall reduced the hydrophobic effect of the PFA tubing leading to small remaining droplets. These droplets caused the same signals in an practically empty tubing as in a filled one. The draining of a used vial could not be detected and the process was stopped with a time-out error.

To overcome the frequent errors an inductive sensor, which had previously been used for an online enrichment system developed by Knapp[39], was used to replace the optical sensor. Although the system was optimized for the use of an 1/8'' tubing it also worked with an 1/16'' tubing. The smaller size of the tubing was used to limit the dead volume of the system. Depending on the acid concentration and the temperature of the sensor wrong readings occurred from time to time but were acceptable compared to the disadvantage of having a higher dead volume. Low acid concentrations reduced the inductive sensitivity whereas temperature changes influenced the electronic components. The use of a carrier solution which contained 40 mL acid per liter increased the sensitivity enough for the inductive determination. Thermal stabilization of the sensor helped to avoid troubles due to wrong readings.

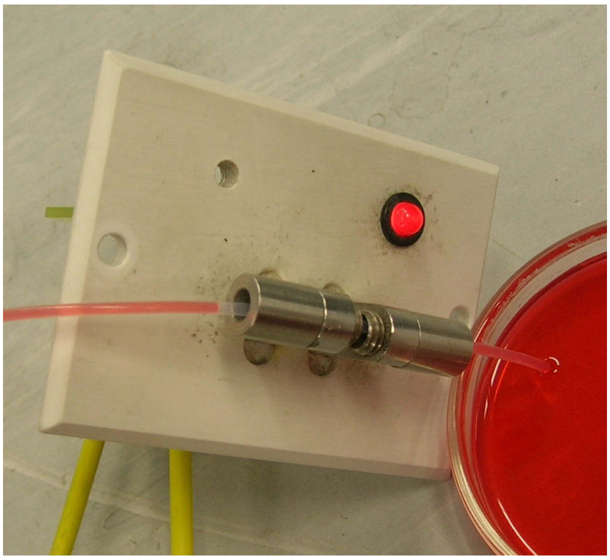


Fig. 6 - 22 Bubble sensor test with detected bubble with a volume of ~ 20 µL

Depending on the pump speed air bubbles starting from 10 µL up to 50 µL could be detected in an 1/16'' tubing with an i.d. of 0.75 mm. The slower the passing bubble was pumped the easier it was to detect it with the sensor. The sensitivity could be adjusted with the help of a potentiometer which was integrated in the electronics behind the white front panel. The two stainless steel sensor parts were used as capacitor plates and changed their capacity dependent on the filling status in the tubing. The changed capacity value tuned an oscillating circuit giving the signal for the detection of liquid and air.

6.5.6 Degasser start-up and leaks

To avoid air bubbles by dissolved air in the acid of the large supply container a degasser was used to prepare a gas-free solution. Without such a device dissolved gases would have escaped due to the low pressure in the suction tubing to the pumps. They would have been collected in the tubing system leading to high pressure pump and stopping the operation as air in the system can not be transported by the high pressure pump. As the used commercial degasser offered four channels two channels in serial connection were used for the carrier supply of the reactor’s high pressure pump. This measure provides safe degassing performance at any pump rate of the system. The two other channels were used to supply each the acid and the sample pump. The chosen model (Gilson 864, Middleton, USA) was made with standard PTFE degasser tubings having a dead volume of 9.2 mL. To reduce the pressure drop through the system a bundle of several 1/16” tubings was used in parallel in the vacuum chamber. The main problem was to start the system again after the supply container had been emptied because the parallel tubings needed a long time to fill completely with carrier again. As the system was designed primarily for solvents the chambers did not withstand the diluted HNO_3 solution. The carrier attacked the glue used to fit the tubings into the connection port which caused leaks after 3 and 4 months of operation respectively. The leaks resulted in air entering the system which stopped the high pressure reactor especially when the carrier container was almost empty. The lower filling level caused more vacuum in the tubing when solution was pumped to the loops. This low pressure led to an intake of air via the leaks in the degasser and finally stopped the process.

6.6 Conclusion

The test container showed the possibilities and performance of an automated digestion system as well as its technical weaknesses and limitations. Running the system 24 hours 7 days a week system failures are imminent due to the high number of components, samples per day and switching actions. Therefore the reliability of the system needed to be improved drastically compared to the tested configuration. Every possible and detected error needed to be eliminated or avoided by increasing the service time and robustness of the components used. To simplify the further development of the digestion system the project was divided into three sections:

- development of a stand-alone digestion system with autosamplers
- implementation of a measuring equipment to run online measurement
- implementation of the digestion and measurement system into a container solution

The next step would only be started after the previous one was solved in all details.

7 Redesign and optimization of the flow digestion system

The frequent interruptions of operation, limited service time of some components and temperature depending system failures needed to be solved in order to increase the reliability of the system. As well as that the simple frame mounted case needed to be replaced with a design fitting to laboratory and process demands. Special attention was also given to the safety regulations which had to be obeyed before the instrument could be released for commercial use.

As mentioned in the conclusion of the previous chapter the further development should be divided into three main sections:
1) the development of the digestion and sample handling system (autosampler)
2) the implementation of a measuring device such as an ICP-OES for online measurement
3) the implementation of the digestion and measurement system into a container solution

7.1 Configurations and features

In every design phase one or two different configurations should be realized offering versatile performance either for offline or at-line sample preparation. With the help of autosamplers or direct connections using at-line filters fully automated sample preparation for liquid samples or slurries should be done. The resulting solutions should then be collected for separate measurement or later be transferred directly to the measuring device without manual sample handling.

7.1.1 Configurations for stand alone sample preparation

Fig. 7 - 1 shows the schemes of the sample collection part of the FDS. In configuration A1 the raw sample is supplied online via a 100 µm filter. The solutions from the reactor are transported to the waste or to the autosampler by means of the collection valve. After diluting the digest with carrier liquid to a set volume in the autosampler cup the valve switches back to the waste port. The autosampler moves to the cleaning station and returns back to the next empty cup in the rack waiting for the next sample. The collected samples are transferred to the ICP for measurement manually.

Configurations A2 and A3 respectively show systems for offline sample introduction. Either two independent autosamplers are used for sample introduction and for sample collection respectively or one sampler needs to have two probes. The advantage of this dual probe solution is the reduced need for additional space and costs.

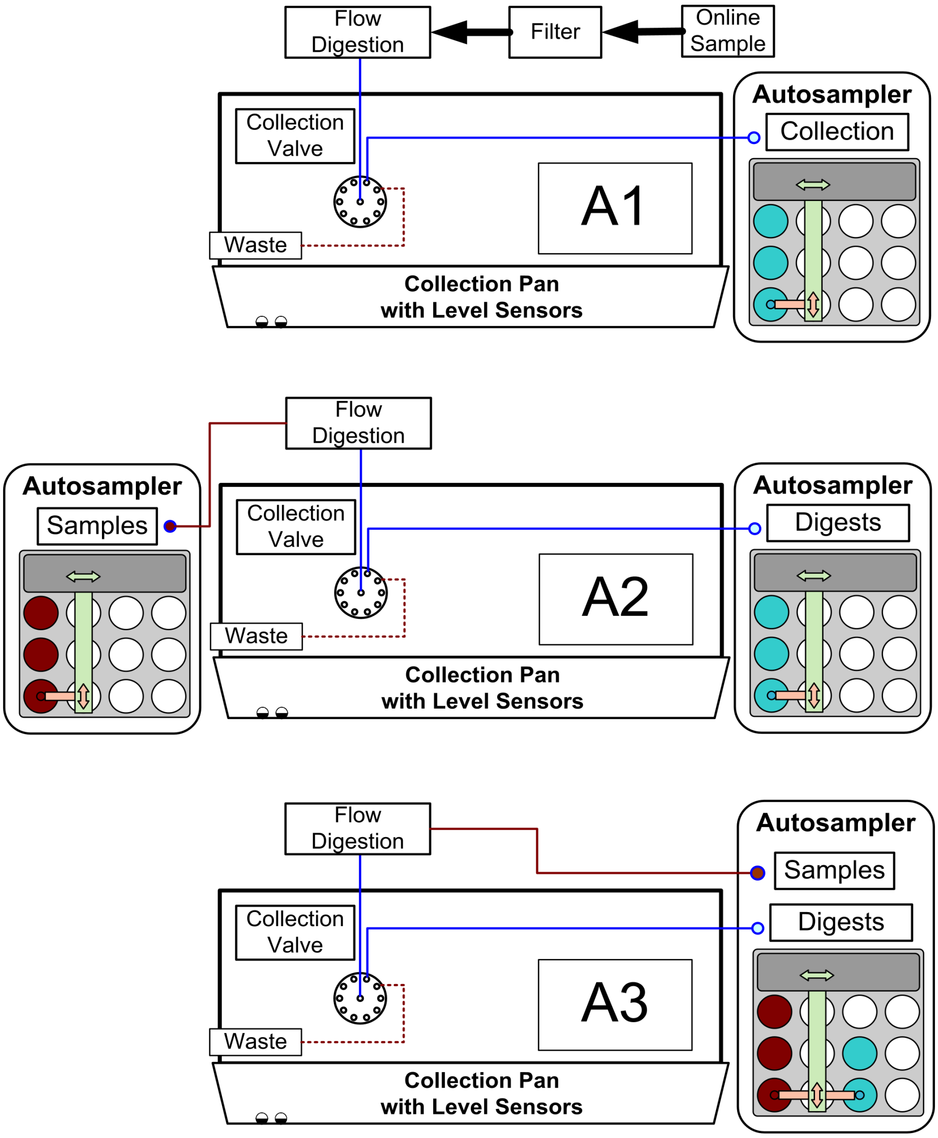


Fig. 7 - 1 Autosampler for at-line digestion (A1) or for sample introduction and collection (A2, A3)

The dual probe version needs minimum two racks, one for the samples and one for the digests. The probes are mounted on one x-y-z-arm of the autosampler. Parallel to the sampling probe a stirrer is mounted to homogenize liquid samples and slurries. While the flow system runs the digestion the autosampler probes are moved to the cleaning station and further on to the next sample and collection vials. While the previous sample is collected the next sample is taken in for digestion. With this configuration up to 120 samples are digested fully automated per day.

7.1.2 Configuration for at-line sample preparation and measurement

The at-line measurement, tested with the prototype of the flow digestion system was only one variation to be realized and tested for the new design. While configurations A1 to A3 in Fig. 7 - 1 only digested samples the two approaches shown in Fig. 7 - 2 intended to measure the samples immediately after digestion.

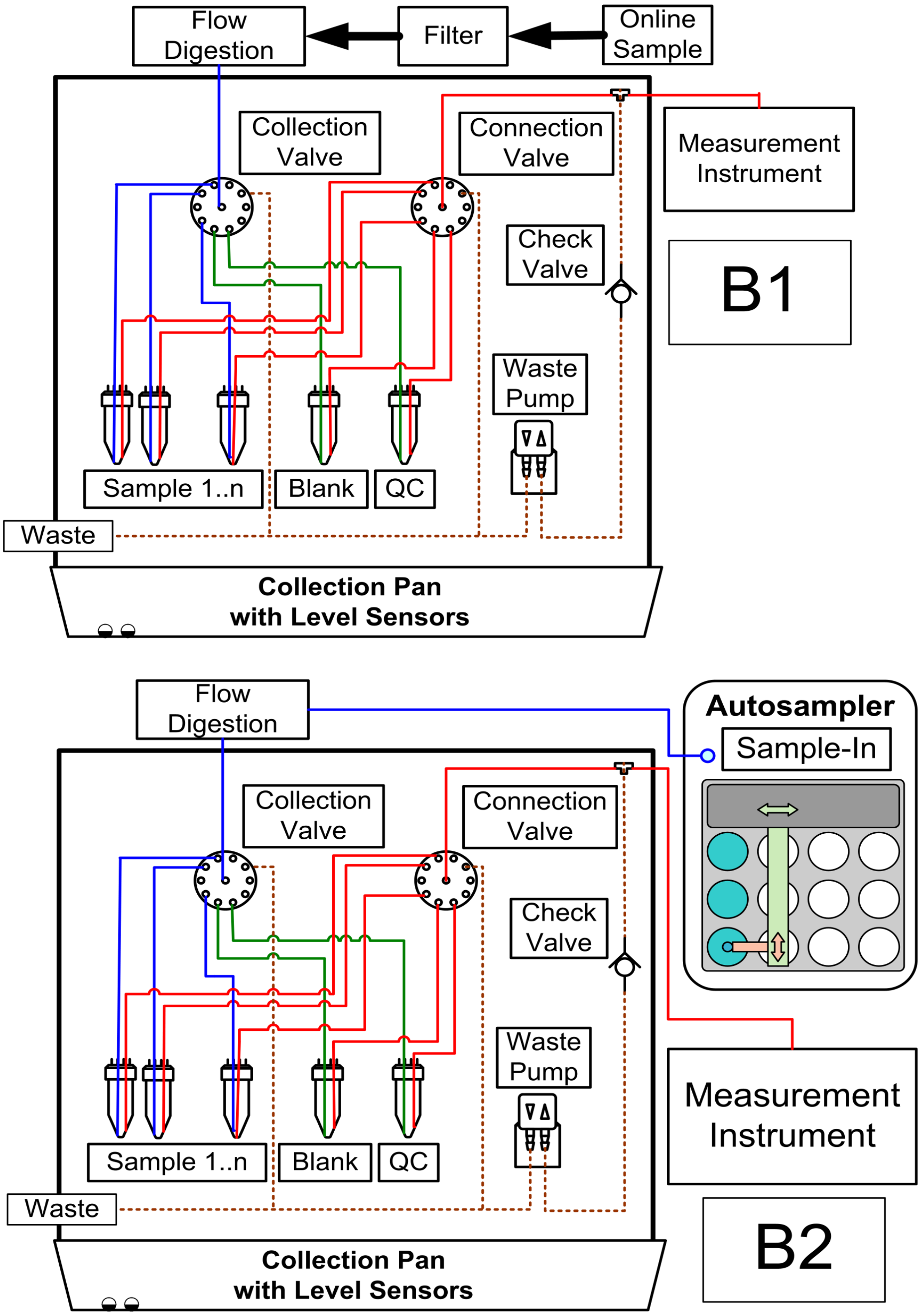


Fig. 7 - 2 Digestion and measurement for at-line (B1) or via autosampler provided samples (B2)

In Fig. 7 - 2 / B1 the scheme of a complete online digestion and measurement mode is shown. Similar to A1 above the sample is supplied via a connected filter unit directly from a sample stream. The digests are distributed to an empty vial by means of the collection valve and diluted with carrier liquid. After diluting the sample to the final volume the collection valve switches back to the waste position. The vial with the diluted digest is connected with the ICP-OES by means of the connection valve. During the measurement the digestion system starts to prepare the next sample and collects it in one of the other vials. To avoid contamination the collection of blank and QC solutions takes place in special vials reserved only for that special solutions.

The synchronization of ICP-OES measurement and digestion process is controlled by a software. After the measuring step has been finished a waste pump removes the remaining sample from the collection vial. A bubble sensor installed in the connection line detects air when the vessel is empty and stops the waste pump. The check valve between the T-shaped fitting and the waste pump prevents the contamination of the digest with waste during measurement. Without the valve it would be possible to pump waste solution or air from the spillage container through the waste pump to the ICP.

After the bubble sensor has stopped the waste pump the connection valve switches back to the carrier port to supply the ICP with diluted acid. The carrier is needed to rinse the connection tubing and the spray chamber of the ICP-OES. At the same time the emptied vial is ready to be filled with the next digestion solutions again. No relevant cross contamination could be observed even though the system had been run without an additional rinsing cycle as the remaining amount of solution was negligible.

The blanks and QC's are handled the same way as the samples, but separate collection vessels are used. Depending on the port number of the connection valve up to five calibration standard solutions can be provided. This solutions are needed to run automated calibration and recalibration procedures of the ICP. The collection pan with level sensors shown in Fig. 7 - 1 is needed to stop the system in case of a leakage during unattended operation.

7.2 Problems and features to be solved for the redesign

The experiments in the container indicated the need for improvements of the digestion system, most importantly the implementation of reliable valve and pump components. Another point for improvement were the bubble sensors as their performance is crucial for process control.

Another points are the requested safety precautions and measures to fulfill international consumer safety regulations. Access to instrument components can not be allowed without having released the pressure to avoid acid spillage on the operator. In addition measures against mechanical endangerment also need to be taken to protect users from moving parts like the pump drives.

Finally all new ideas to improve handling, servicing and analytical performance of the system are included in the redesign phase to offer a reliable system. This not only included a user interface software allowing easy access to all system parameters, methods, sample lists and service functions but also the implementation and synchronization of measuring equipment. In Table 7.1 the list of all necessary improvements, functions and safety adaptations are listed with comments.

Table 7.1: List of optimization tasks for the basic flow digestion system

	Components	**Problems**	**Goals**
1	6-Port distribution valve	leaking due to abrasion and chemical attack	resistance against abrasion & chemical corrosion; more ports
2	Bubble sensor	low sensitivity for 1/16” tubing, temperature sensitivity	detection of small bubbles in 1/16” tubing, robust against temperature changes
3	Sample and acid pump	leaks at low temperature; limited service time of the PTFE piston	robust against temperature changes, longer service time, additional port for rinsing solution
4	Degasser	difficult to start with empty lines due to large dead volume; air leaks at the fittings	shorter and less tubing, higher degassing efficiency and robust fittings
5	PTFE-TFM liner in the reactor tubing	strong deformation during startup and pressure drops leading to limited service time	liner adapted to the supporting tube, still usable with standard 1/16” components.
6	Injection valve	abrasion, difficult servicing, valve drive too large	improved sealing material, easier replacement or maintenance and smaller size
7	Waste pump	linear membrane pumps leak when running on air frequently	self-priming pump with eccentric membrane drive for permanent dry operation
8	Reactor isolation	glass wool is difficult to apply properly during reactor change	solid isolation foam for easy installation and constant isolation properties
9	Vapor protection	escaping vapor needs to be extracted	safety valves and switches needed to stop the process for service
10	Component interface	large variety of interfaces needed to connect to the control unit	one standard module offering different hardware interfaces; connected via a bus system
11	Software	control only via the development tool of the controller (w/o GUI)	user-friendly control GUI-software to operate the digestion and measurement device
12	Autosamplers	tests only with a single autosampler without rinsing	operation of one or two autosamplers; at- or offline mode including probe rinsing

7.3 Low pressure distribution valve experiments

To overcome the described problems with the distribution valves three other models were tested in comparison. For the performance experiments the same sample solution which had been applied during the experiments in the container was used. The salt, acid and particle concentration destroyed the Cavro Smartvalves in relatively short time due to abrasion and chemical attack of the rotor holder. The new components should show their superior performance when run at similar conditions.

The following valve components were ordered for the comparison test:

- Vici Cheminert 10-port PTFE/PEEK with motor drive (Vici, Schenkon, Switzerland)
- Hamilton 8-port PTFE / Aluminum with valve drive MVP (Hamilton, Bonaduz, Switzerland)
- Rheodyne TitanEX PEEK/Kel-F 10-port with integrated drive (Rheodyne, Oak Harbor, USA)
- Cavro Smart Valve 6-port Aluminum/Kel-F/PTFE with drive module (Cavro, Sunnyvale, USA)

As the last three valves were delivered late the Vici valve was used before the verification for a dry switching test and experiments with water filled lines. During the dry test the PTFE rotor in the valve was damaged after 170,000 switching actions (see Fig. 7 - 3). The abraded material was found all over the valve and was even pressed out of the central port. After replacing the switching rotor a test with water filled connection tubings was performed with 79,000 cycles. In this test both parts, the PTFE rotor and the PEEK stator did not fail due to the lubricating effect of the water filling. The valve was used after inspection without service for the comparison experiments together with the other valve units.

Fig. 7 - 3 Vici Cheminert Valve: massive PTFE abrasion after 170,000 dry switching experiments

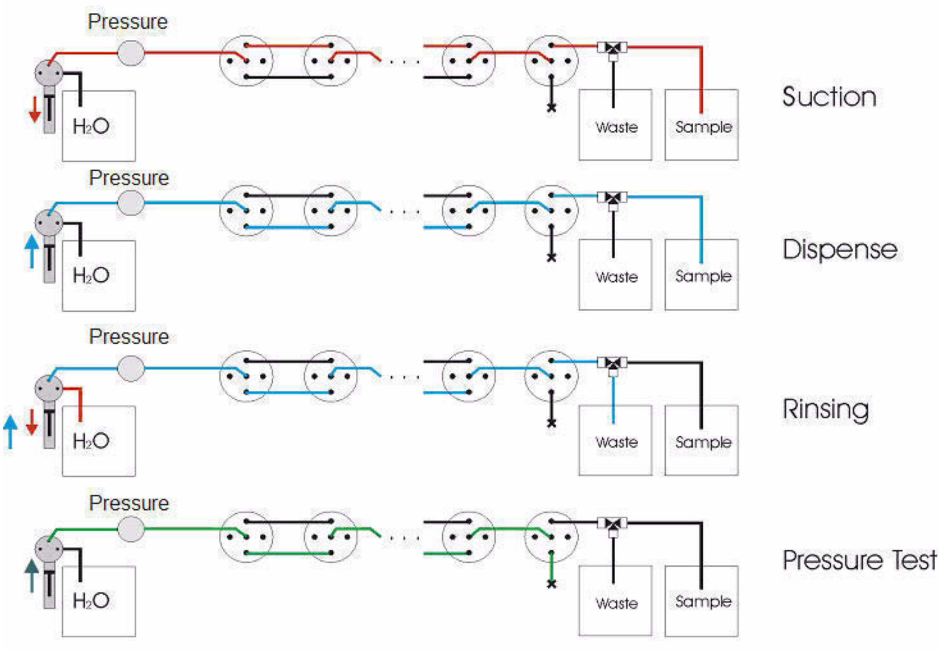


Fig. 7 - 4 Flow chart for the valve test with pump, pressure sensor and sample & waste container

The goal was to make the operation as real as possible. The valves were filled with the sample slurry by sucking it from a container with the help of a syringe pump (red arrow and lines in Fig. 7 - 4, "Suction"). After filling the valves with the samples the valves repeatedly switched their positions before the pump dispensed the slurry back into the sample container (blue line in Fig. 7 - 4, "Dispense"). Frequently the valves were rinsed with water connected to the sample pump. The magnetic valve guided the rinsing solution to the waste container (red and blue line in Fig. 7 - 4, "Rinsing"). On demand the system did a pressure test by using water which had been pumped against a closed port on the last valve in the line (see Fig. 7 - 4, "Pressure Test"). The pump slowly increased the control pressure to 3000 mbar. The new valves were able to keep the pressure above 2950 mbar for typically 400 s after the pump had stopped.

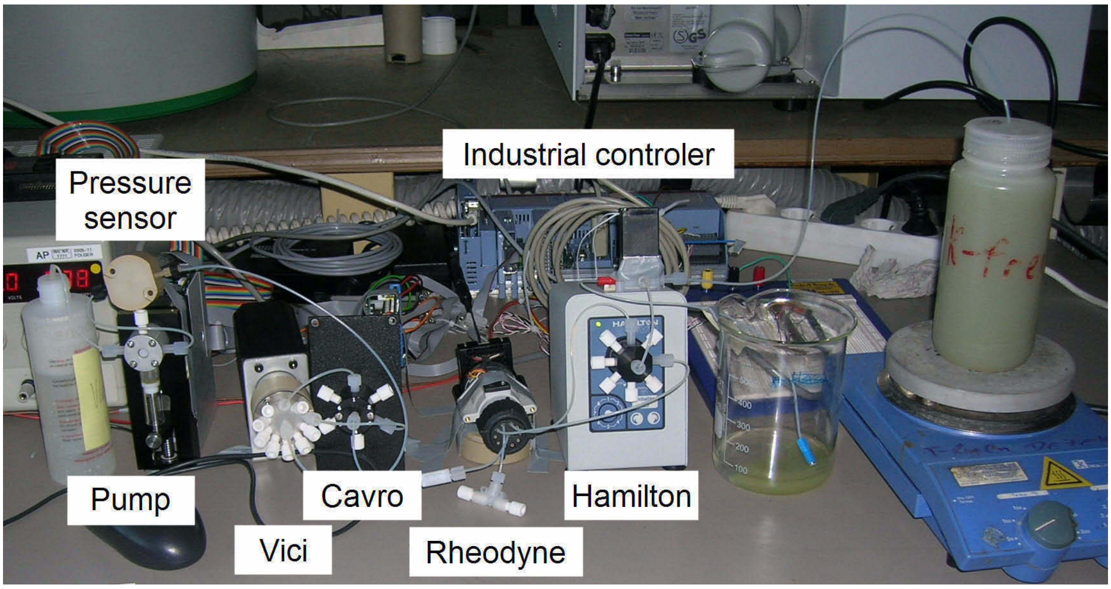


Fig. 7 - 5 Valve test setup with sample container on a magnetic stirrer and industrial controller

The test setup was controlled by the same industrial controller which had been used in the first prototype (B&R, Eggelsberg, Austria). The sample slurry was mixed with a magnetic stirrer to maintain the suspension. An electronic pressure sensor (Keller, Winterthur, Switzerland) was needed for the tightness experiments.

In case of passed pressure experiments the system continued the next switching cycles. A failure of the pressure test stopped the test procedure allowing to check for the problem.

7.3.1 Test procedure

The test period was 3 weeks during which one after the next valve dropped out of the performance test. The complete experiments ended after leakage had been detected on the last two units as well. The following steps were programmed for the operation of the test valves:

Filling the valves with sample:	new sample for every trial
Switching between two ports after filling:	10 times
Purging the sample:	pump sample back in the mixed container
Rinsing with water:	after 20 sample cycles
Pressure test:	manually every day

Table 7.2: Valve failures and pressure performance during the valve test

Cycles	**Comment**	**time / -50 mbar**
0	New valves, after 10 pressure experiments	400 s
5,000	Pressure did not reach 3 bar; leak on Hamilton valve	--
123,054	Cavro Valves leaks on neighbor ports after plugs had been removed	< 1 s

Leakage of the Hamilton valve

After only 2 days and 5000 cycles the first leakage was detected on the Hamilton valve. It is designed similar to the Cavro valve with a conical PTFE Rotor in a Kel-F body. The leakage was dramatic as sample solution could not only be found all over the valve body but also in the drive unit itself. Strong abrasion of the PTFE rotor and the leak below the valve drive can be seen in Fig. 7 - 6 and Fig. 7 - 7.

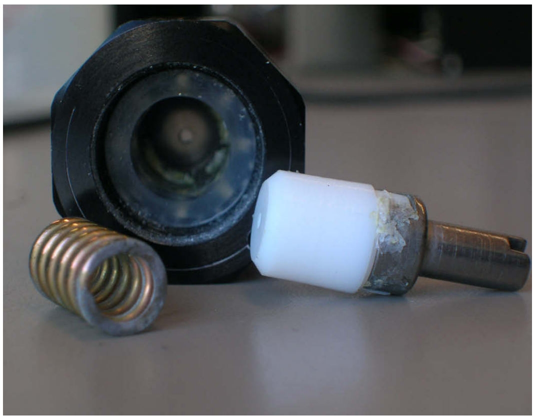


Fig. 7 - 6 Detailed Hamilton valve showing abrasion of the rotor

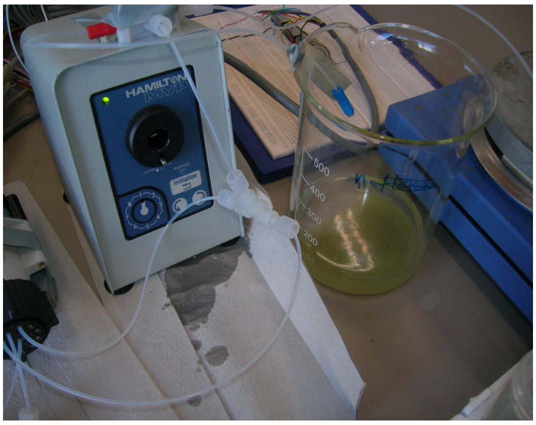


Fig. 7 - 7 Strong leakage of the Hamilton 8-port valve drive

Leakage of the Cavro valve

After one week and 123,054 switching cycles respectively the Cavro valve needed to be replaced. Before the manually initiated pressure test the white blind plugs (see Fig. 7 - 5) were removed from the neighbor ports that had not been used. Without plugs it was possible to see the sample leakage on the empty ports during the pressure test and the pressure dropped from 3000 mbar to 2950 mbar in less than one second.

In Fig. 7 - 8 the groove around the conical rotor, causing the leakage to the neighbor ports is indicated by red arrows. The permanent movement of the rotor caused the abrasion of PTFE and is highlighted in the same picture by the black arrow.

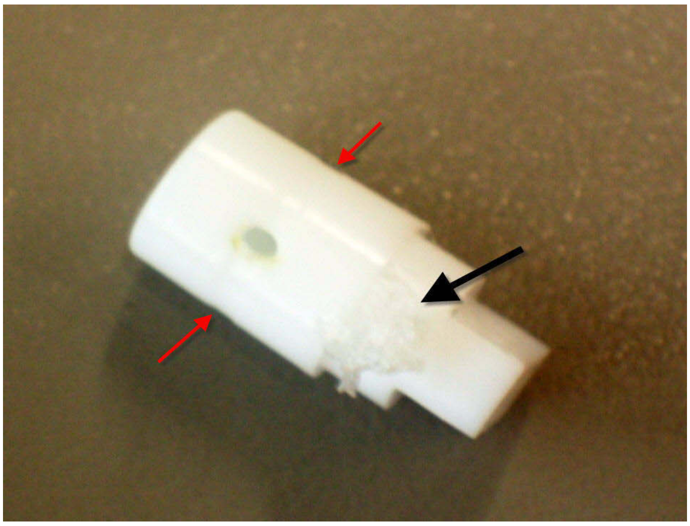


Fig. 7 - 8 Cavro rotor with groove (red arrows) and abrasion from the PTFE body (black arrow)

Continued experiments with Vici and Rheodyne valves

After the two conical seal valves had been removed from the system setup the test continued for additional two weeks with a pressure test every day. After more than 300,000 cycles had been reached for the first time a pressure test was done to determine the influence of the pump. Although a sample loop had been used some particles managed to enter the pump causing abrasion on the pumps piston. The goal was to determine how long the pump alone can maintain the pressure. For this test the two valves were disconnected and the connection port on the pressure sensor was blocked by a plug. The time of the pressure drop was compared with the time of the complete setup (see Table 7.3).

The valve test ended when leaks were detected at the open Rheodyne ports during the pressure test which had been done after 347,870 switching cycles. To verify the influence of the different components on the pressure test every valve was tested independently after the pump had been verified again. As can be seen in Table 7.4 the pump performance remarkably decreased after 301,000 cycles compared to the performance at the test start. The main leak came from the Rheodyne, but partially also from the Vici valve.

Table 7.3: Pressure performance during and at the end of the valve test (drop of 100 mbar)

Cycles	**Comment**	**time / -100 mbar**
301,868	Pressure test with pump, Vici and Rheodyne	5 s
301,868	Pressure test only with the pump	60 s
347,870	Pressure test with pump, Vici and Rheodyne	1 s
347,870	Pressure test with pump and Vici	6 s
347,870	Pressure test with pump and Rheodyne	2 s
347,870	Pressure test only with the pump	14 s

Table 7.4: Valve performance at the end of the valve test at 2000 mbar (drop of 100 mbar)

Cycles	**Comment**	**time / -100 mbar**
347,870	Pressure test with pump, Vici and Rheodyne	26 s
347,870	Pressure test with pump and Vici	46 s
347,870	Pressure test with pump and Rheodyne	31 s

The peek pressure of the dispensing system should be limited to 3000 mbar while the normal working pressure will not exceed 2000 mbar. Therefore the valves were also tested at lower pressure limits to see if the effects are linear to the applied pressure. A decrease of the test pressure to 2000 mbar (-33%) increased the time needed for a 100 mbar pressure drop 26 times. Such a performance would still be acceptable for normal operation and would help to increase the service time of the components. During inspection following alterations of the valves were found:

Rheodyne TitanEX:

The TitanEX is not designed to be serviced by an operator, but with special care and the help of another person it was possible to disassemble the unit. The disk-design is similar to the valve from Vici. A rotor with a grooving from the center to the rim connects the tubing from the center port with one of the ports surrounding it. A disk spring package intensively presses the rotor to the stator which contains the tubings. This is necessary to avoid leaks in case of higher pressure in the system.

Due to this force the PTFE rotor disc showed abrasion after the experiments, but the empty ports were not blocked by PTFE particles. The valve body did not show sample residues; the leaking sample left the valve via the open neighbor ports.

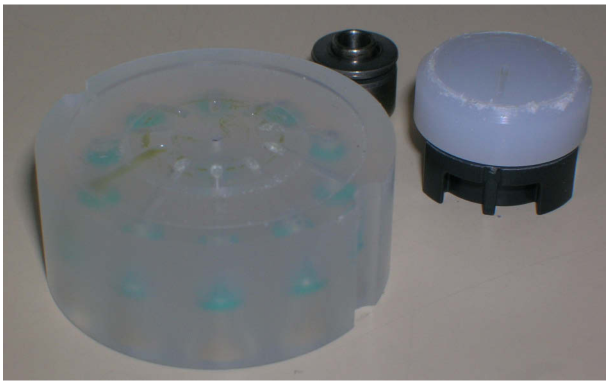


Fig. 7 - 9 Rheodyne TitanEX Kel-F stator (left) and PTFE rotor (right)

After cleaning the Kel-F stator and the PTFE rotor were polished in the Anton Paar machine shop and then reassembled. The pressure test performed at 3000 mbar after the service resulted in pressure dropping times for 50 mbar at above 400 seconds.

Vici Cheminert:

The Vici valve is build to be serviced, but for the price of a much larger footprint, large fittings and a three times higher price for the unit including the motor drive. The spring package is stronger compared to the Rheodyne valve. This is why the PTFE is pressed to the stator with enormous force. After disassembling the rotor showed heavy wear and the open ports of the stator were blocked by PTFE particles. The metal rotor holder was at the same height as the PTFE part, but due to a grooving around the stator sealing surface the metal did not damage the stator. The valve body was dry and did not show sample residue.

Fig. 7 - 10 Vici Cheminert rotor with spring package (left) and Kel-F stator (right)

Due to obviously softer materials the stator and the rotor did not show groovings like the corresponding parts from Rheodyne. After cleaning with water and paper and rinsing the ports with a syringe the valve was reassembled with a new rotor disk. The pressure test showed the same performance at 3000 mbar as it had before the complete test cycles.

7.3.2 Service time calculations

The time needed to collect the sample and dilute it typically limits the number of samples. Using the optimized procedure with 2.5 mL flow rate and 25 mL collection volume it took 10 min to digest one sample. The sample uptake and acid mixing needed additional time but could be parallelized with the second sample after the system start. With six samples per hour the system was theoretically capable of running maximum 144 samples. In routine operation with rinsing times 130 samples per day were the best number that could be achieved. With a smaller volume of samples the amount of collected digestive could be reduced. Even with that measure the number of samples did not exceed 150 digestions.

Sample valve switching actions

During one standard digestion the sample valve needs to switch seven times. In Table 7.5 the different steps are shown in detail.

Table 7.5: Switching actions of the sample valve during a normal digestion process

Step	Port	Action
1	Air	Load separating bubble
2	Sample	Pre-rinse sample tube with the next sample
3	Waste	Drain the sample solution used for rinsing
4	Air	Load a new air bubble
5	Sample	Load the sample solution
6	Mixing-T	Mix the sample with acids and load the injection loop
7	Waste	Drain remaining sample and air bubble and rinse the tubing

Compared to the high number of samples per day the switching actions during the system start can be neglected. With 350,000 tested switching actions one valve should be able to operate one year and still offer an acceptable performance.

Calculation of expected service time for the sample valve:

$$\text{Days of operation} = \frac{\text{number of tested switching actions}}{\text{samples per day } \times \text{switches per sample}} = \frac{350{,}000}{130 \times 7} = 385 \text{ days}$$

Acid valve switching actions

The number of switching actions for the acid valve may vary depending on the acid mixture used and the number of mixing steps and fractions respectively. The mixing before the digestion is necessary for nitric and hydrochloric acids. Premixtures of the acids tend to form gaseous products leading to difficulties to dispense them properly. On the other hand it is no problem to mix hydrofluoric and hydrochloric acid and supply this mixture in case siliceous particles are included in the sample. In Table 7.6 the different steps are shown in detail for a mixture of two acids and a fractionation in four sections. When using only one acid for digestion the number of switching actions is reduced from 16 to 11 rotor movements skipping step 7 to 11 in the list.

Table 7.6: Switching actions for the acid valve during a normal digestion process

Step	Port	Action
1	Air	Load separating bubble
2	Nitric Acid	Load separating acid plug
3	Int. Std.	Load 50% of internal standard solution
4	Nitric Acid	Load first fraction of nitric acid
5	Acid 2	Load first fraction of acid or acid mixture 2
6	Nitric Acid	Load second fraction of nitric acid
7	Acid 2	Load second fraction of acid or acid mixture 2
8	Nitric Acid	Load third fraction of nitric acid
9	Acid 2	Load third fraction of acid or acid mixture 2
10	Nitric Acid	Load fourth fraction of nitric acid
11	Acid 2	Load fourth fraction of acid or acid mixture 2
12	Int. Std.	Load 50% of internal standard solution
13	Nitric Acid	Pre-rinse sample tube with the next sample
14	Mixing-T	Mix the sample with acids and load the injection loop
15	Waste	Drain remaining acids, the air bubble and rinse the tubing

For the acid valve the number of theoretical operation days is shorter because of more switching actions for each sample. On the other hand the valve never is in contact with solutions containing abrasive particles. This drastically increases its life time. Therefore the lifetime was in practice not shorter as the lifetime of the sample valve as observed with the first prototype.

Calculation of theoretical service time for the acid valve:

$$\text{Days of operation} = \frac{\text{number of tested switching actions}}{\text{samples per day} \times \text{switches per sample}} = \frac{350{,}000}{130 \times 15} = 179 \text{ days}$$

Collection and connection valves switching actions:

The collection and connection valves only need to switch twice per sample. There are no abrasive particles in the solutions which reduces the service time. Compared to the sample valve the two components should operate at least three years without changing the system.

7.4 Bubble sensor

For the precise control of the flow system a reliable bubble or air indication is important. The capacitive sensor used in the prototype was already an improvement compared to the optical sensor, even though temperature stability and sensitivity were not good enough for a reliable operation. It was necessary to determine an air bubble with 10 µL volume in a 1/16'' tubing with an i.d. of 0.75 mm pumped at a flow rate of 3 mL/min. Converted to other units it is necessary to detect a bubble with a length of 20 mm flowing at a speed of 100 mm/sec. Having a sensor with 40 mm in length the bubble has a residence time of only 0.2 s.

A dielectric change inside the tubing would alter the capacity of the sensor tubings. The metal sensor tubes are part of an oscillatory circuit which tunes a frequency generator. An air bubble of the requested size causes a frequency change of around 10 % when distilled water is used and 20 % if diluted acids or salt solutions are used. Another parameter was the flow speed: the slower an air bubble passes the sensor the easier is it to determine a difference between a filled or an empty tubing. The signal was determined by the change of the frequency using a fast counter in the sensor electronics. This counter was also responsible for another positive side effect of the new design. The sensor signal was always the relative difference between the frequency of the filled and the empty tubing eliminating thermal or tube material effects. Offering a self-optimization routine the sensor could be optimized for different tubing and reagent materials eliminating wrong sensor readings.

7.4.1 Performance test

To test the reliability of the new designed sensor two electronic boards were tested at the same time. For the preparation of a liquid stream with air-bubbles a two channel peristaltic pump was used. One channel with a larger pump tubing was used to produce a liquid stream, the second channel with different smaller pump tubings supplied different amounts of air bubbles. The signals of the boards were analyzed with the help of the industrial controller which had already been used in the valve experiments. The controller checked the number of bubble counts that came from the two different sensors connected to each other (Fig. 7 - 11).

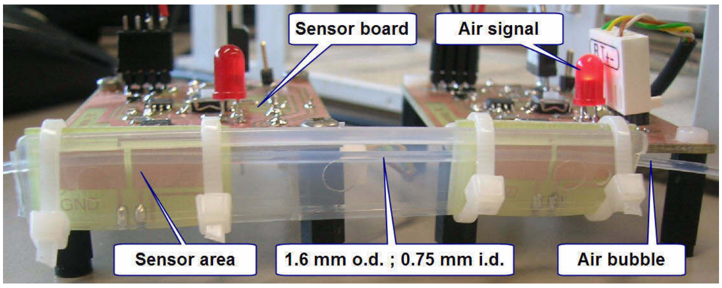


Fig. 7 - 11 Bubble sensor parallel test setup with air bubble indication

The new sensor boards were able to determine bubbles down to a volume of 10 µL at a flow rate of 3.5 mL. For performance experiments the two pump tubings (Reglo Digital, Ismatec, Glattbrugg, Switzerland) were adjusted to supply approximately 10 % of air bubbles in a carrier stream. The sum flow rate of both pumps was set to 3.0 mL using a carrier with 0.5 M HNO_3. The results after 72 h of permanent operation including temperature changes between 15℃ and 30℃ are shown in Table 7.7. The controller measured the time for the two different signals, carrier and air. As can be seen the bubble signals only differed less than 0.3 %; an excellent value for a prototype setup.

Table 7.7: Bubble detection rate for 72h of permanent operation with varying ambient temperature

Sensor	Signal Carrier [ms]	Signal Air [ms]	Air [%]
Prototype 1	228239370	33578910	12,82
Prototype 2	228935780	32882500	12,56

7.5 Sample and acid pump

The Cavro pump used in the prototype was replaced by the IPV pump module of Sapphire, Oak Harbor, USA (Fig. 7 - 12). The sapphire piston and the rinsed sealing ring of the displacement pump were responsible for the high number of pump actions. In addition the pump was less sensitive for changes in temperature and the installed disc valve with ceramic parts promised long service times, too.

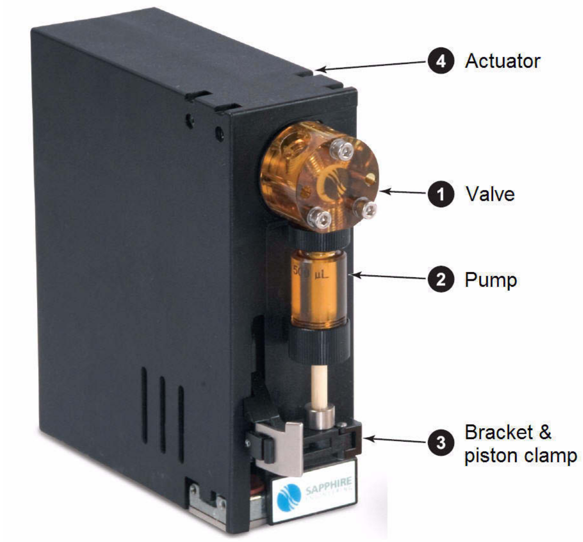


Fig. 7 - 12 Integrated pump and valve module (IPV) from Sapphire, Oak Harbor, USA

The integrated pump and valve (IPV) module shown in Fig. 7 - 12 have only two ports. For the new design a similar 3-port version with 2.5 and 5.0 mL pistons was used. The wetted parts consisted of Sapphire, Al_2O_3- ceramic, Kel-F and Ultem which offered extremely high resistance against corrosion and wear. The included drive software commands are compatible to the Tecan modules used before offering easy exchange of the hardware.

7.6 Degasser

During the prototype test a standard four channel degassing system with large degassing chambers was used. The design included porous PTFE tubing bundles fixed to one connector in a vacuum chamber to release dissolved gas. The sealing and fixation of the tubing bundle in the connector was damaged due to a diluted nitric acid attack. The resulting leak caused system stops due to air bubbles in the high pressure system. Another problem was the large dead volume of the tubing: a restart after emptying the system was time consuming because it was difficult to remove all the air from the chamber.

For the optimized configuration, new degassing chambers were tested which took advantage of extremely porous tube materials. One single short 1/16” hose made of amorphous PTFE copolymer (Teflon AF) offered the same degassing performance like a bundle of several long tubings in standard chambers. The chamber with the largest dead volume had 925 µL offering 70% degassing at a flow rate of 2.0 mL/min (Mini degassing chamber, Rheodyne, Oak Harbor). Two chambers in serial connection were used to provide perfect solutions for the high pressure line. One single chamber for each dosing pump avoided that air bubbles influenced the dosing precision. The tubing inside the chamber was connected with the same flangeless fittings used for other 1/16” PTFE tubing in the system avoiding sensitive sealing glues.

For the vacuum supply a zero hysteresis - constant run pump (ZHCR, Rheodyne, Oak Harbor) was used together with a control board with vacuum sensor and the motor drive electronics. The assembly can be seen in Fig. 7 - 13 except for the printed circuit board which is separated for corrosion protection.

The additionally shown bubble trap was designed to remove large gas bubbles like CO_2 or NO_x from the digest once the system is connected to an ICP. The chamber removes large bubbles more efficient than the degassing chambers can do. A solenoid valve was used to disconnect the chamber for an operation without an ICP instrument. A vacuum sensor at the control board allowed to operate the pump only at needed minimum speed level to increases the service time of the complete setup.

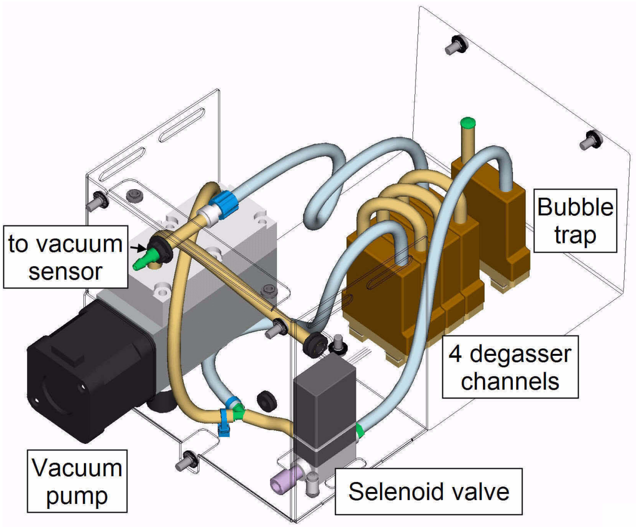


Fig. 7 - 13   Degasser, debubbler and vacuum pump as 3D model

7.7 Injection valve

The injection valve has to switch only twice for every digested sample. Abrasive particles in the sample stream still harmed the system by the enormous force the rotor and stator disks are pressed together. Nevertheless the service time of the injection valve during the prototype test was acceptable because particles were removed from the valve by the acid plugs before switching the valve ports.
A smaller valve drive footprint, higher acceptable operation pressure combined with easy replacement service were the attributes of the new injection valve used for the new design. The Titan HT (Rheodyne, Oak Harbor, USA) offered a pressure stability of up to 1000 bar, but for the price of higher friction and wear. To allow long time operation the working pressure was reduced to 450 bar. This value gave still

some remaining reserve compared to the limited operation pressure of 220 bar. The easily removable and affordable liquid end valve head (also called POD) was used in the new design to reduce the time needed for a service replacement. The disassembled valve can be seen in Fig. 7 - 14.

Fig. 7 - 14 Liquid end (POD), drive and quick-fix screw for the Titan HT injection valve

7.8 Waste pump

During the test of the prototype three different approaches were used to remove the remaining digest in the collection vial in online digestion mode:

1. a peristaltic pump with a large dimension silicon tubing (i.d. of 1/8“)
2. a magnetic piston oscillating pump with a fluorinated membrane
3. an eccentric diaphragm pump with a fluorinated membrane

Version 1) is the most expensive solution with a very good self priming but short service time of the pump tubings in the range of maximum several weeks. The advantage of the pump is the relatively high resistance to dry operation of the tubing.

Version 2) was the cheapest solution with high pump rates, but had difficulties with dry starts (self-priming) and only short service times due to the frequently operation without liquids in the pump. The reason for damages is the high amplitude of the magnetic piston in an empty pump. Missing liquids allow maximum oscillation without attenuation destroying the pump’s membrane (see Fig. 7 - 15).

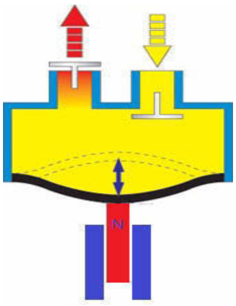


Fig. 7 - 15 Schema of a magnetic piston membrane pump with air and liquid medium

The motor driven eccentric membrane pump of version 3) (KNF Flodos, Wassermatte, Switzerland) was expensive but offered unequaled service time. The eccentric drive does not change the membrane's amplitude running with or without sample. Another positive effect is the relatively slow oscillation frequency extending the service time to minimum 6 months. Besides it is very easy to replace the diaphragm to service the pump module. Typical pump time per sample: 30 s

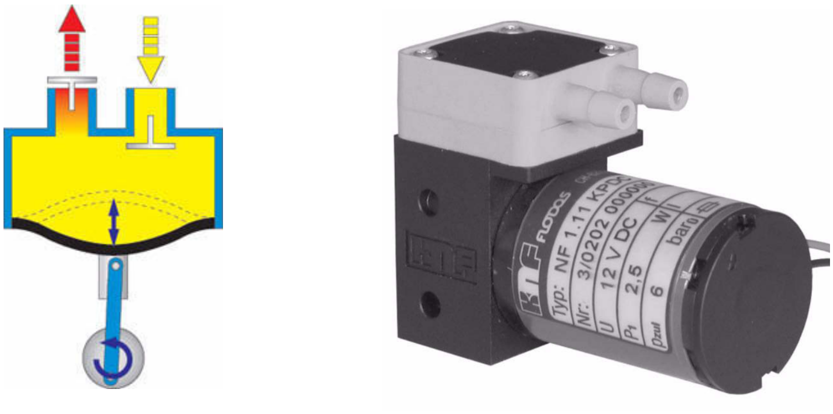


Fig. 7 - 16 Schema and picture of the motor driven eccentric membrane pump

7.9 Reactor isolation

To reduce the needed wattage for reactor heating and to avoid burns the reactor needed to be isolated. The touchable metal surface temperature should not exceed 60°C and the isolation material should be reusable for several reactors. Wrapping the reactor with glass mats was easy, but after two or three reactor coil changes the material lost its shape and insulation efficiency. In case of a reactor leak the mat was soaked with huge amounts of reagents before the solution started to be drained and detected by the leakage sensor.

To improve handling and service time a solid isolation material was chosen to replace the flexible glass wool. Glass foam, like the one used for technical and constructive thermal isolation was found to be most useful compared to other solid isolation materials like firebricks. It could be easily machined to a shape to encapsule the hot reactor. The closed pore design avoided soaking effects seen for the glass mat and the material is available at low costs due to large scale production for construction applications.

As the material tends to crumble the isolation block was mounted in an easy access stainless steel case. The operator only has to open the case with the build-in isolation material without having to touch the glass foam.

It is only a question of five minutes to open the isolation, remove the old reactor and reinstall a new reactor including complete isolation. In Fig. 7 - 17 the open reactor isolation is shown. The shown glass mat parts had previously been used as sealing material between the different foam parts. Comparison experiments have shown that the additional isolation effect of this glass mats was negligible. For further experiments the parts were removed for easier handling.

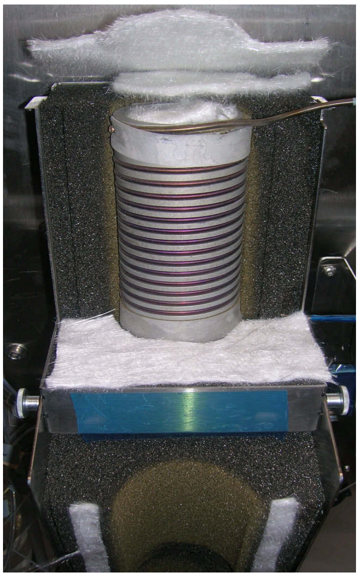


Fig. 7 - 17 Reactor coil with glass foam isolation and the isolation steel case

In Fig. 7 - 17 an applied blue plastic film stripe can be seen. This stripe is necessary for proper IR measurement as plastic materials have a very high IR emission rate of 0.97. For steel the emission factor is much lower and reflection from the environment can take place. The impressive effect of the thin stripes is clearly demonstrated in the IR picture of Fig. 7 - 18. The hottest spot is near the mounting area of the heating core on the isolation bottom part. The blank steel surface shows an almost 30℃ lower temperature although the system is heated homogeneously. The efficiency of the isolation was proven by this IR-measurement of a reactor running at 300℃ for 12 hours. The temperature indicator on the right side shows that the requested limit of 60℃ was not exceeded on any position of the reactors isolation shell.

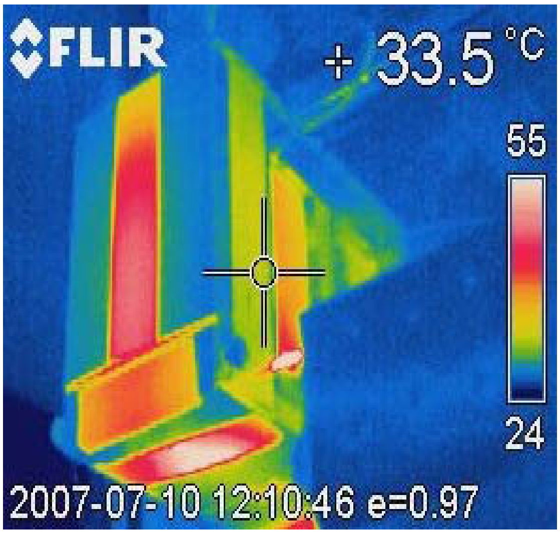


Fig. 7 - 18 IR-Temperature measurement of the isolated reactor running at 300°C for 12 hours

7.10 Vapor and acid spillage protection

In case of a reactor or tube leak the build-in exhaust system needs to remove all acid vapors. At the same time the venting system is needed to cool the reaction coil, the reactor casing and the electronic and drive components. Protection shields or covers are needed to prevent acid or sample spillage onto the operator while inspecting the running system. The prototype had only one shield in front of all components and no active venting except the cooler.

For the new instrument design a new approach was needed. For easy operation and servicing the system was divided into two sections needing separate venting and cooling situations. It should be possible to access the sample and acid pumps or valves as well as the collection and distribution components without stopping and cooling the reactor. A separate cover should enclose the high pressure components like the high pressure pump, the injection valve and the reactor with the back pressure regulator. The other components are less susceptible for leaks and will not release large amounts of acid vapor.

In a 3D model the air guiding channels, separated for the high pressure part and the other dosing equipment are shown (Fig. 7 - 19). The venting slits can be seen in the front view, the air guides as well as the exhaust fan are shown in the back view. The air intake is integrated in the bottom and supplied with a filter to avoid airborne dust contamination inside the system.

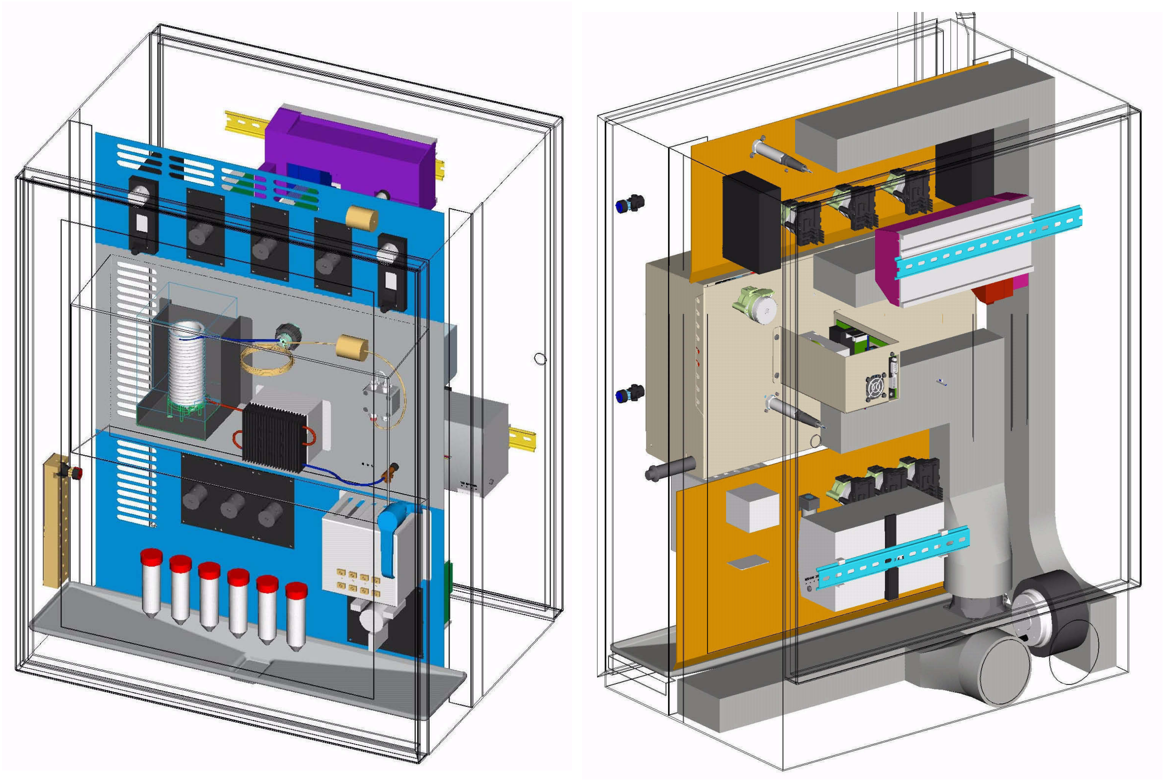


Fig. 7 - 19 Ventilation system of the digestion unit: front and back view as 3D model

7.10.1 High pressure protection cover

The cover of the high pressure components needs to be locked to avoid operators access without complete depressurization of the area. To ensure automatic venting the cover was closed by a screw connected to a safety valve. This measure ensured that the high pressure cover can only be opened after a complete pressure release. The enclosure also supported the safe exhaust of acid vapors. In case of a leakage the complete reactor content gets fully vented. In the small volume of the protection cover it is easier to extract the vapors compared to the large volume of the complete system.

For the proper dimensioning of the venting system the amount of vapor produced by a reactor failure needed to be measured. For that purpose a test was necessary to determine the volume of gas remaining after expansion and cooling. Not all carrier or acid will escape in gaseous form as the stored energy in the overheated water is not high enough to evaporate all of it. A part of the acid vapor produced will condensate during expansion due to cold surfaces and cooling effects. In the worst case volume can be calculated using only water as carrier. The lightweight molecule forms more vapor than any diluted acid solution does.

Water weight in the reactor m:	10 g
Water temperature T_2:	300℃
Specific evaporation enthalpy of water h_{we}:	2257 kJ/kg
Specific enthalpy of water h_{wl}:	4.19 kJ/kg℃

Energy content E available in 10 g overheated water at 300℃ for evaporation at T1 = 100℃ into normal atmosphere pressure:

$$E = m \times h_{wl} \times \Delta T = 0.01\ \text{kg} \times 4.19\ \text{kJ/kg°C} \times (300 - 100\ \text{°C}) = 8.38\ \text{kJ}$$

This amount of energy can evaporate m_{ev} water at 100℃ at ambient pressure

$$m_{ev} = \frac{E}{h_{we}} = \frac{8.38\ \text{kJ}}{2257\ \text{kJ/kg}} = 0.00371\ \text{kg} = 3.71\ \text{g}$$

As a first approximation this amount of water corresponds to a final steam volume V_{ev} of:

$$V_{ev} = V_n \times \frac{m}{MG_w} = 22.414\ \text{L/Mol} \times \frac{3.71\ \text{g}}{18\ \text{g/Mol}} = 4.62\ \text{L}$$

This relatively small amount of steam, reduced by additional condensation on cold surfaces inside the protection cover will not cause critical pressure peaks. The effect is additionally limited as the volume of the cover will include more than 30 L. Another positive effect is the venting time normally in the range of three to five seconds. Therefore the resulting pressure increase is easy to manage.

To prove the theoretical calculations a leakage test was done breaking a short sample injection loop inside a collection bag. Due to the direct connection without check valve the reactor's content was able to release at the broken end. The bag's volume was 3.5 L and closed by means of a grip seal. After heating the reactor to 300℃ at 150 bar the loop was cut with a knife. The escaping steam-water-mixture filled the bag almost completely within the mentioned 3 to 4 seconds, but did not manage to open the grip sealing. It could clearly be seen that liquid was released from the first opening together with the steam. The complete test was repeated twice with the setup shown in Fig. 7 - 20.

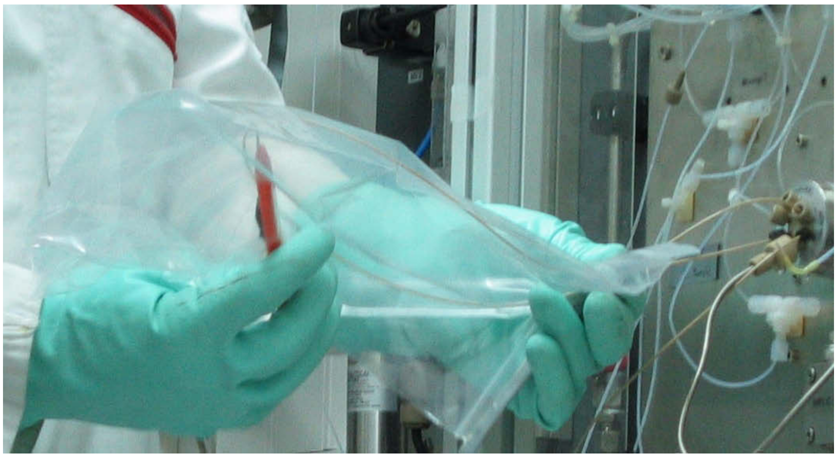


Fig. 7 - 20 Hot venting test after a tubing breakage

7.10.2 Safety release valve

The reactor breakage experiments have shown that the cover manages the protection of the operators safely during maintenance works on the low pressure components. An additional safety venting valve in the connection line between the reactor and the injection valve should release the system's pressure in case an operator opens the cover. Before accessing the high pressure units the reactor should normally cool down completely. After that the pressure can be released via the backpressure regulator. In a system blocked by solid particles this may not be possible. In such a case the safety valve can be used to release the pressure safely and conveniently. The main purpose of the valve, however, is to prevent the opening of the high pressure fittings without discharging the reactor which leads to burns by the vented reagents.

Three venting experiments were done for the safety valve releasing a completely heated reactor into a collection bottle connected to the valve. The valve and the bottle as well as the cover can be seen in both, open and closed position, in Fig. 7 - 21.

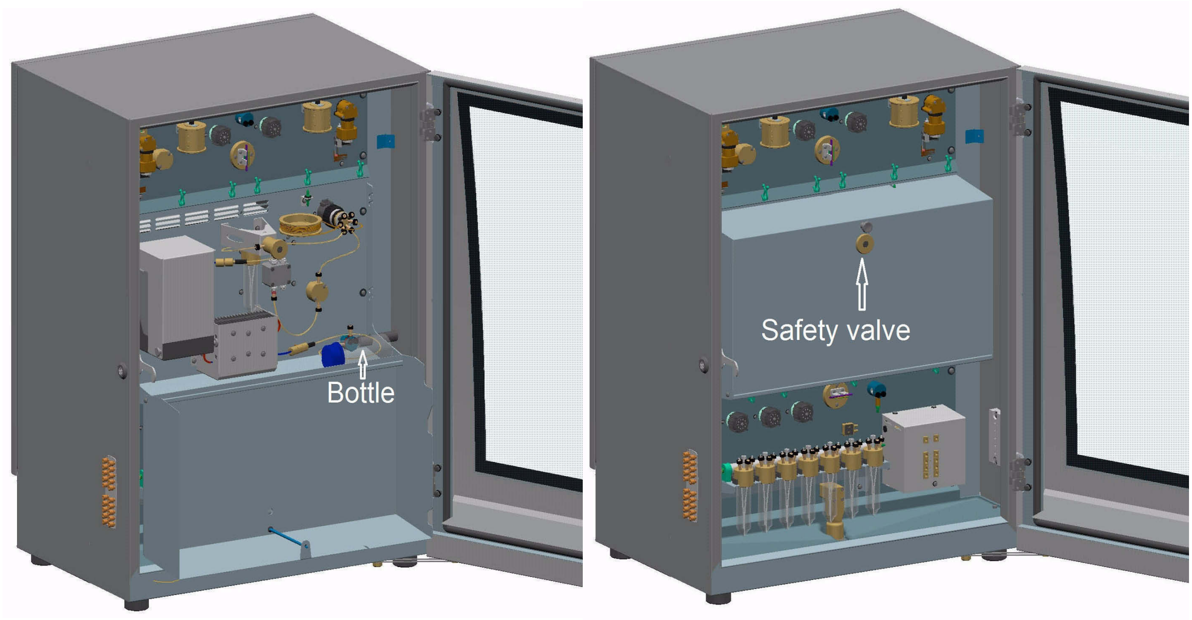


Fig. 7 - 21 Position of the safety valve, a reclined bottle (PP) and the protection cover (open/closed)

The valve allowed a controlled release and the collection bottle avoided acid spillage in the system which cannot be avoided in case of a broken tubing. The maximum temperature reached while venting was determined again by means of an IR measurement. In Fig. 7 - 22 two pictures, taken two and six seconds after opening the safety valve, are shown. The maximum temperature (107℃ after 2 seconds) did neither exceed the limits of the PTFE-TFM connection tubing nor the ones for the PP collection bottle.

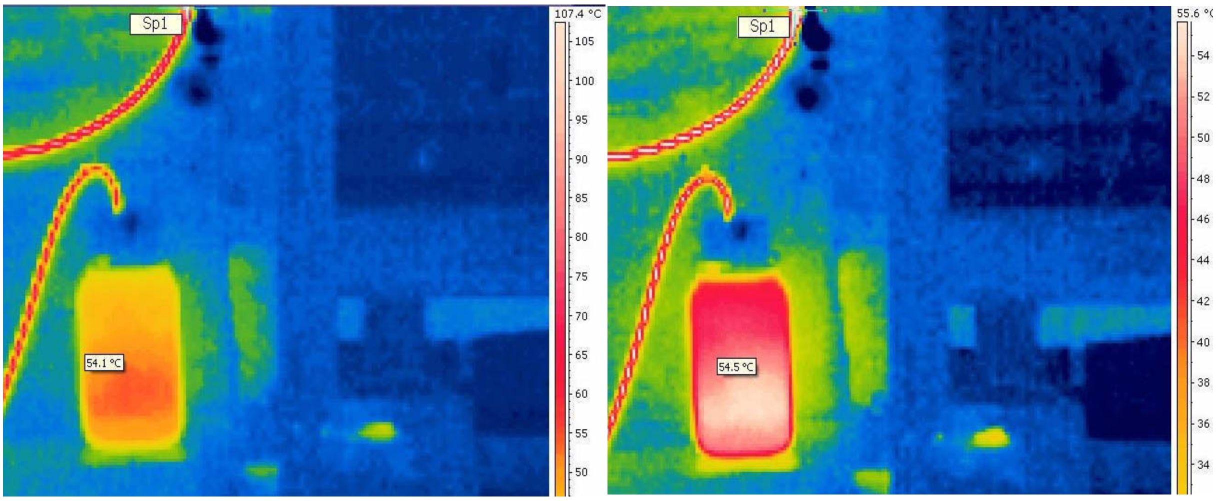


Fig. 7 - 22 IR-temperature measurement for the safety valve venting and the collection bottle

7.11 Component interface

The integration of multiple components in one large automated system needs special measures to maintain full communication with all members. In parallel the design needs to be flexible to allow unforeseen modifications in the future for system upgrades or allow the replacement of components with new communication needs.

The prototype system's controller consisted of a commercial microprocessor with all optional communication modules needed for control of the used components.

For serial production of the new design the costs for this additional expensive parts needed to be reduced. Because the new valves needed too much digital ports it was technically necessary to use one central digital input/output unit for controlling. In the first stage following communication ports needed to be realized:

Table 7.8: Needed connection boards for the complete flow digestion system

Amount	**Component**	**Port**
2	Pump-valve module	RS 485
4	10-port distribution valve	BCD digital I/O
1	Injection valve	BCD digital I/O
1	High pressure pump	RS 232
2	Autosampler	RS 232
2	Pressure sensor	Analog
2	Temperature Sensor	Pt 100
1	Safety Center (safety switches)	Digital in
2	Bubble Sensor	Digital in
1	Degasser vacuum error	Digital in
1	Reactor heating	Digital out
1	Waste pump	Digital out

To fulfill all communication needs and to maintain a high level of flexibility a versatile adapter print with a variety of different input/output features was designed. The included microprocessor and firmware allows future upgrade of the features and possibilities. In case the upgrade can not be done by means of a new software a new version of the cheap adapter can be installed. This solution is much better than a replacement of an expensive communication module of the industrial controller.

For the communication between the different adapters and the central control unit the CAN-bus technology was used. The fast communication protocol is also installed for many automotive applications. The mass production for the car industry gives low prices compared to other control hardware techniques. Using the CAN bus the number of adapters can easily be increased to provide additional features necessary for example to install the unit in a container.

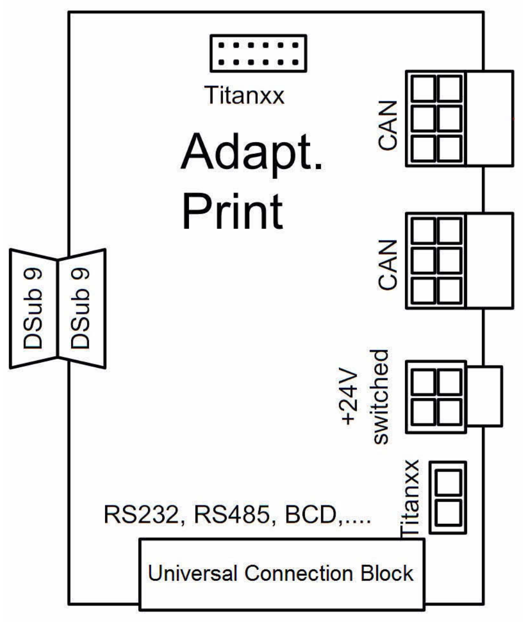


Fig. 7 - 23 Adapter print with communication and power supply connectors

The new adapter covered all BCD digital I/O which were needed for the valves, the RS 232 for the high pressure pump and the autosamplers as well as RS 485 ports for the pump-valve-modules. The two CAN sockets are used to connect the incoming and outgoing bus cables. The power supply with 24 V not only supplied the adapter but also the valve and pump modules. For the TitanEX valve the corresponding 2-pin socket can be seen on the board, other components are supplied via the universal connection block.

The separately shown sensors and the single digital in- and out-ports shown in Table 7.8 are connected to the central control unit. The basic control module has already provided these kinds of ports in the standard configuration avoiding the need to implement them in the adapter board.

The build-in controller of the adapter board allowed to implement the specific control details for the different valves and pumps like a driver for the main process management. Changes in the configurations can be done easily via a driver update, the core program remains untouched.

7.12 PC control software

The complicated operation of the prototype needed to be replaced with one simple graphical user interface (GUI). This software package should manage the digestion system, the autosamplers, the basic ICP instrument commands as well as the environmental control of the container at the end of the development.

7.12.1 Software design and features

VisioLab was the software environment also used for other PC applications at Anton Paar. The package based on Dot.Net provided all general tasks like method loading, editing, saving and printing. It was extended by detailed configuration tabs allowing to enter all relevant parameters that were needed for digestion and measurement. The working title for the software package was VisioLab FDS.

The main element of the program was the sample and methods list. The methods defined the amount of reagents, samples, collection volumes, all the different pump rates and pressure or temperature limits. The sample list provided information on the digestion and measurement schedule. It included the position of samples in the autosampler, the number of digestions before the next control blank or control sample as well as the schedule for recalibrations if an ICP was used.

The digestion system and the autosamplers are controlled from VisioLab FDS via the included industrial controller in the flow digestion system. For the ICP monitoring an ABI (application binary interface) for the ICP control software was needed to communicate with the FDS-GUI. Via this ABI commands are send to start the ICP and the needed calibration and measurement tasks. The same channel was used to inform VisioLab about finished measurements, passed or failed quality control checks or other important information from the measurement.

7.12.2 Software modules

The software consists of five main modules:

- the configuration module
- the method module
- the sample list module
- the monitoring module
- the environmental module

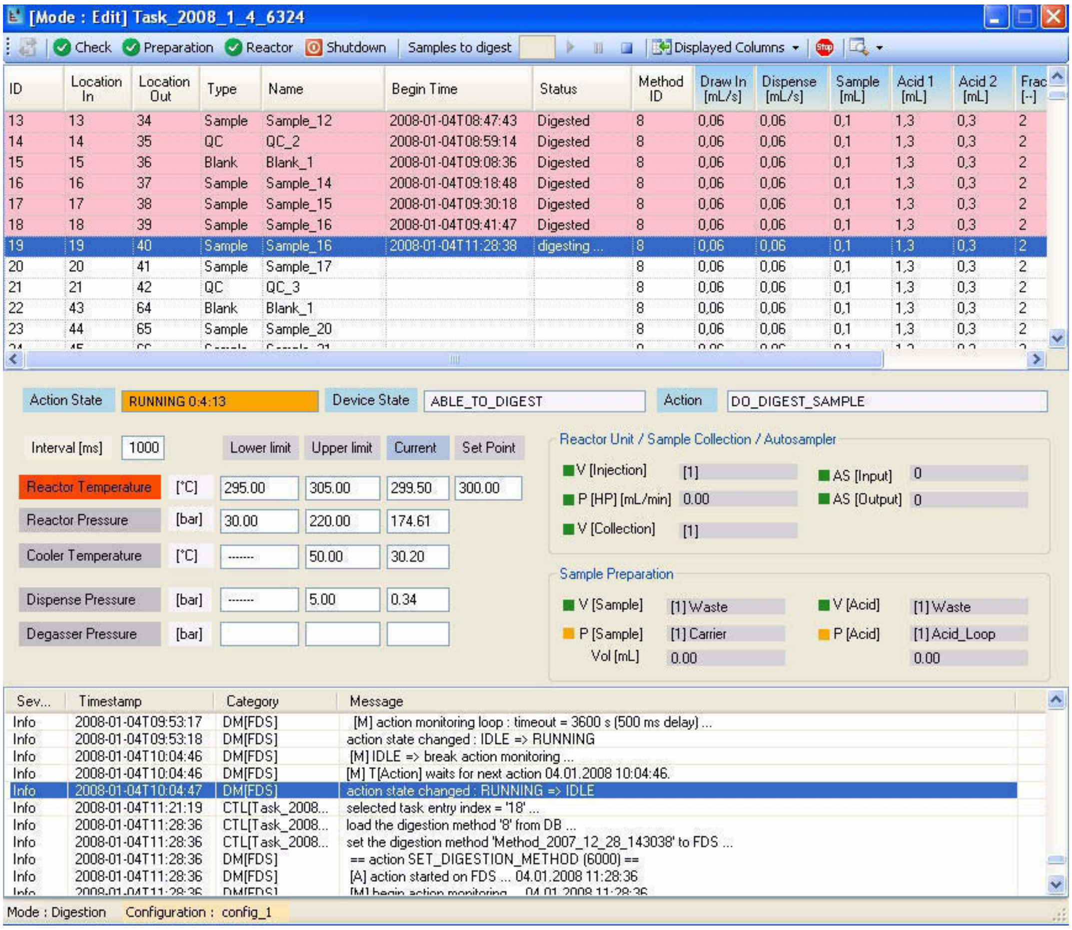
While the first 4 modules are necessary for the basic functions the environmental module was only drafted. In table Table 7.9 the basic functions of each module are described.

Table 7.9: Software modules and their functions

Module	Function	Notes
Configuration	Basic system options	setup defining the connection to online filter, autosamplers or ICP
	Pump and valve configuration	pump module's volume & speed, port connections, tubing & reactor lengths
	Startup and error handling	definition of startup-, shutdown- and error handling routines
Methods	Digestion methods	definition of reagent and sample amounts, standards and QC samples
	Regular maintenance routines	setup for cleaning, calibration and QC cycles; measures after QC or blank failures
Sample list	Digestion sequence	list of samples and their position in the autosampler and the corresponding method
	Method optimization	running similar samples with different methods from the same or different containers
Monitoring	Liquid handling	valve port positions, dosing pressure, bubble sensor signals
	High pressure reactor	reaction pressure and temperature, time to collection end
	Autosampler	actual position and running autosampler action: rinsing, mixing, moving or collection
	Message log	window showing a log file of past actions, warnings or error messages

7.12.3 System monitoring

The screenshot in Fig. 7 - 24 shows the monitoring view of the VisioLab FDS software. The sample list is shown while running a digestion using an autosampler with a dual probe (see configuration A2 in Fig. 7 - 1). While the sample and acid valves prepare a new solution with the sample on position 19 the reactor and the collection valve digest the sample from position 18. The digest gets collected and diluted into the vial on position 40. The blue line in the screenshot indicates the sample in preparation. Preparation of the sample means the sample uptake, acid mixing and loading of the mixture into the injection loop. The pink lines above the blue line are already finished, the lines below are waiting for processing. In addition all reactor parameters and valve settings are monitored and indicated in the middle section. In the lowest section of the control screen a log list shows the different steps of the program with time stamps for the documentation.



ID	Location In	Location Out	Type	Name	Begin Time	Status	Method ID	Draw In [mL/s]	Dispense [mL/s]	Sample [mL]	Acid 1 [mL]	Acid 2 [mL]	Frac [--]
13	13	34	Sample	Sample_12	2008-01-04T08:47:43	Digested	8	0,06	0,06	0,1	1,3	0,3	2
14	14	35	QC	QC_2	2008-01-04T08:59:14	Digested	8	0,06	0,06	0,1	1,3	0,3	2
15	15	36	Blank	Blank_1	2008-01-04T09:08:36	Digested	8	0,06	0,06	0,1	1,3	0,3	2
16	16	37	Sample	Sample_14	2008-01-04T09:18:48	Digested	8	0,06	0,06	0,1	1,3	0,3	2
17	17	38	Sample	Sample_15	2008-01-04T09:30:18	Digested	8	0,06	0,06	0,1	1,3	0,3	2
18	18	39	Sample	Sample_16	2008-01-04T09:41:47	Digested	8	0,06	0,06	0,1	1,3	0,3	2
19	19	40	Sample	Sample_16	2008-01-04T11:28:38	digesting ...	8	0,06	0,06	0,1	1,3	0,3	2
20	20	41	Sample	Sample_17			8	0,06	0,06	0,1	1,3	0,3	2
21	21	42	QC	QC_3			8	0,06	0,06	0,1	1,3	0,3	2
22	43	64	Blank	Blank_1			8	0,06	0,06	0,1	1,3	0,3	2
23	44	65	Sample	Sample_20			8	0,06	0,06	0,1	1,3	0,3	2

Action State: RUNNING 0:4:13
Device State: ABLE_TO_DIGEST
Action: DO_DIGEST_SAMPLE

Interval [ms]: 1000

		Lower limit	Upper limit	Current	Set Point
Reactor Temperature	[°C]	295.00	305.00	299.50	300.00
Reactor Pressure	[bar]	30.00	220.00	174.61	
Cooler Temperature	[°C]	-------	50.00	30.20	
Dispense Pressure	[bar]	-------	5.00	0.34	
Degasser Pressure	[bar]				

Reactor Unit / Sample Collection / Autosampler
V [Injection]: [1]
P [HP] [mL/min]: 0.00
V [Collection]: [1]
AS [Input]: 0
AS [Output]: 0

Sample Preparation
V [Sample]: [1] Waste
P [Sample]: [1] Carrier
Vol [mL]: 0.00
V [Acid]: [1] Waste
P [Acid]: [1] Acid_Loop
0.00

```
Sev...  Timestamp            Category          Message
Info    2008-01-04T09:53:17  DM[FDS]            [M] action monitoring loop : timeout = 3600 s (500 ms delay) ...
Info    2008-01-04T09:53:18  DM[FDS]           action state changed : IDLE => RUNNING
Info    2008-01-04T10:04:46  DM[FDS]            [M] IDLE => break action monitoring ...
Info    2008-01-04T10:04:46  DM[FDS]           [M] T[Action] waits for next action 04.01.2008 10:04:46.
Info    2008-01-04T10:04:47  DM[FDS]           action state changed : RUNNING => IDLE
Info    2008-01-04T11:21:19  CTL[Task_2008...  selected task entry index = '18' ...
Info    2008-01-04T11:28:36  CTL[Task_2008...  load the digestion method '8' from DB ...
Info    2008-01-04T11:28:36  CTL[Task_2008...  set the digestion method 'Method_2007_12_28_143038' to FDS ...
Info    2008-01-04T11:28:36  DM[FDS]            == action SET_DIGESTION_METHOD (6000) ==
Info    2008-01-04T11:28:36  DM[FDS]            [A] action started on FDS ... 04.01.2008 11:28:36
```

Mode : Digestion   Configuration : config_1

Fig. 7 - 24 Sample list during a digestion using a dual probe autosampler

As long as the system did not start the preparation it is possible to enter new lines or modify the list. The possibility to enter different methods within one sequence can be used for optimization routines. Samples can be treated with different amounts of acids, different acid mixtures or reaction conditions. Using that option the system can automatically verify and quickly get the best digestion conditions.

7.13 Operation with autosamplers

In the first part of the system's development the focus was on a stand-alone digestion solution without online sample connection and ICP measurement. The goal was to improve and stabilize the digestion system before other steps are taken. To allow the simple and efficient optimization of the method and the system autosamplers were used for the automated performance verification routines. Both offline autosampler configurations shown in Fig. 7 - 1 (A2 and A3) were realized. The version with two autosamplers needs more space but allows to run more samples without reloading the system. The used dual probe sampler comes with 4 racks, each having 21 vials with 50 mL. That means a maximum of 42 samples can be processed before the operator needs to reload the racks. The normal autosamplers used for configuration A2 are using the same rack size and can therefore handle twice as many samples as the dual probe version is able to run without supervision and manual container replacement.

7.13.1 Autosampler for offline operation

The experiments were done with modified autosamplers supplied by Cetac, Omaha, USA. The standard sampler ASX 520 was used for configuration A2 and had special corrosion protection on the metal drive rails (see Fig. 7 - 25)

Fig. 7 - 25 Autosampler ASX 520 for single probe operation used in configuration A2

For configuration A3 with dual probes a special version of the heavy duty sampler ASX 1400 was used. In addition to the similar corrosion protection of the rails a collection tray under the racks, a second probe holder and a second rinsing station were also applied (see Fig. 7 - 26).

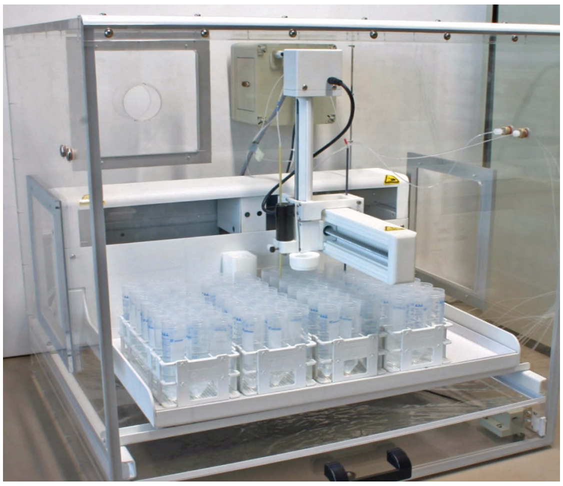


Fig. 7 - 26 Autosampler ASX 1400 with dual probe holder, stirrer and protection cover

The probes were made of PFA tubing reinforced by a metal free carbon fiber tube. The stirrer consisted of a PFA covered titanium tube. To avoid dripping from the sample and the stirrer while driving over the other positions to the rinsing station a drip cup swivels under the two units as soon as the probes are on the upper position. The probe, the stirrer and the drip cup can be seen in Fig. 7 - 27.

Fig. 7 - 27 Dual probe holder with stirrer and drip cup for the ASX 1400

To mix the samples with the carrier during dilution the collection probe dips into the solution. The gas bubbles resulting from the digestion carefully stir the solution. To avoid cross contaminations from one sample to the other it is necessary to rinse the collection probe while the sampling probe and the stirrer are rinsed. That is why a second rinsing station needed to be installed on the sampler. The two stations are shown in Fig. 7 - 28.

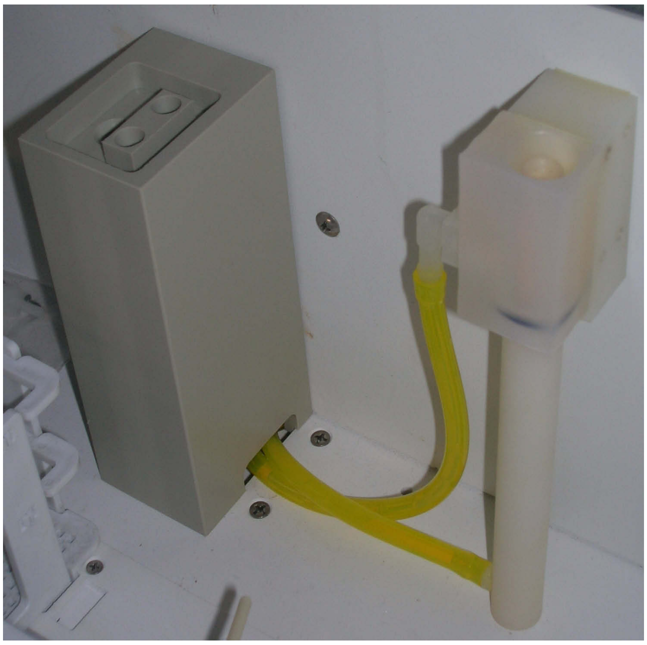


Fig. 7 - 28 Rinsing stations for the sample probe and stirrer (left) and collection probe (right)

7.13.2 Protection and exhaust case

The powerful motors of the autosamplers results in a certain risk for the operator of getting insured when handling sample vials during running processes. Another risk is coming from the toxic nitrous gases that escape from the collection vials while digestion runs. Last, but not least the lab needs to be protected against acid spillage in case the system does not collect the samples properly. All security needs can be solved with a closed cabin for the autosampler.

Safety interlocks in the door interrupted the power supply when the door was opened. When connected to an exhaust system the toxic and acidic vapors are collected and removed. A tray underneath the sampler can collect acid or rinsing solution. At the same time a level sensor mounted in the tray would stop the process. The designed box with the sampler is shown in Fig. 7 - 26. Another positive analytical effect was the limitation of airborne contamination as the box was equipped with an air inlet filter.

8 Digestion system performance verification

After all optimization steps had been implemented and the new features had been developed, three test units were built up to verify the system's performance, stability and reliability. In addition to the hardware development the needed soft- and firmware packages were prepared to start experiments using a configuration either with two different autosamplers or one sampler with the dual probe solution.

8.1 Pilot production units

The picture below (Fig. 8 - 1) shows one pilot production unit after assembly at the factory at Anton Paar. The system did not include the options for online coupling, but all relevant pumps and valves needed for offline sample digestion of liquid samples and slurries. The configurations also included all safety features like leak detection level switches, exhaust cabins for the autosamplers with protection trays and interlock switches for the doors.

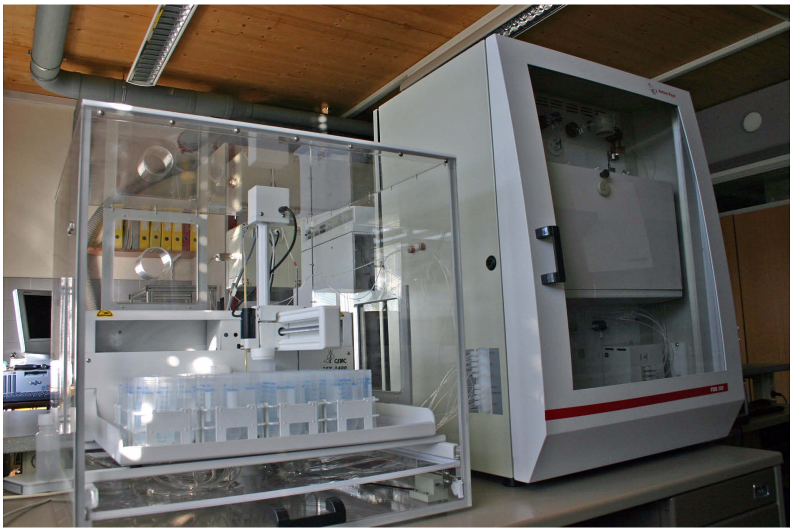


Fig. 8 - 1 Flow digestion system pilot production with autosampler and exhaust cabin

The picture of the digestion system with open front cover shows the sample dosing components and the closed cover for the high pressure unit which is shown in details in Fig. 8 - 2. On the lower left corner a fitting block with 20 connection ports made of PTFE has been installed. This block was used to supply the system gas tight with the needed solutions, samples and reagents. In the lower part the sample collection valve can be seen together with the degassing unit and the leakage detection level switch. The small waste pump was only installed for test purposes as it is only needed for online measurement configurations.

Fig. 8 - 2 Offline flow digestion system with open front door showing pumps, valves and loops

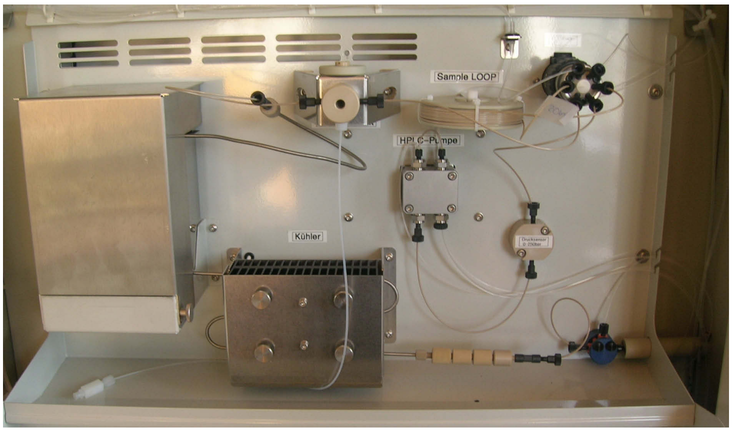


Fig. 8 - 3 High pressure reactor components behind the protection cover

The high pressure components are covered with a protection shield and locked with a screw which is attached to the safety venting valve (see Fig. 8 - 3). The collection bottle attached to the safety venting hose is not shown in the picture, but was used for the experiments. After the cooler the special high pressure fitting can be seen together with additional three extension parts. These extension fittings are needed to allow the maintenance of the reactor in case of needed cleaning and inspection.

After the flangeless fitting was disassembled it is not possible to insert the used reactor tubing into the fitting again due to expansion. On the contrary it slips into the supporting titanium sleeve. Therefore the extension fittings are needed. When one of the fittings is removed it is possible to fix the PTFE-TFM tubing behind the fitting with fingers or a pair of tweezers and push it through the flangeless fitting. After the parts are assembled again the excessing length of the PTFE-TFM liner hose needs to be shortened to have 2 mm length out of the fitting. This is the only way to avoid a complete reactor replacement once the fitting has been removed for cleaning.

For easy service and maintenance similar components are used inside the system. In addition to the pumps and valves many cables as well as the adapter boards mentioned in the section before could be used on several different positions in the system. Only few spare parts are necessary to be able to repair the unit without ordering new parts. A big service door on the backside of the instrument allows the fast replacement of components in case of a failure.

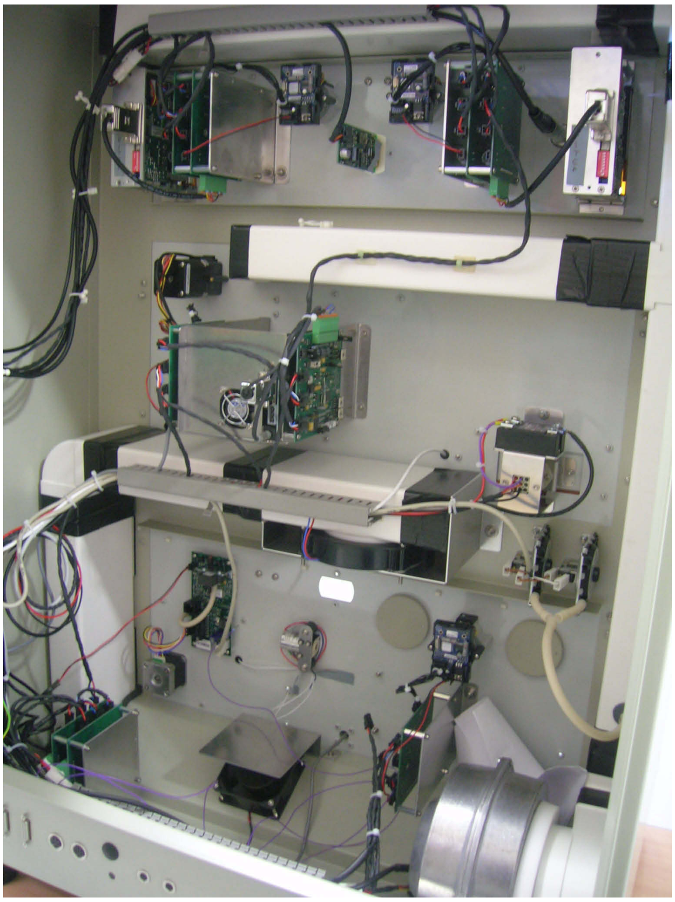


Fig. 8 - 4 Easy access to the electric and electronic components in the service compartment

8.2 System installation and initialization

The three test units should be verified according to the following list:

- Installation of all tubings and leakage tests with water
- Test and optimization of the startup routines
- Test of normal and alarm shutdown behavior
- Digestion test runs using water as reagents, carrier and samples
- Digestion test runs with reagents using water as sample with autosampler
- Digestions with real reagents, carrier and waste water samples

8.2.1 Installation of all tubings and leakage tests with water

After the complete assembly of the flow digestion system with all valve and pump modules it was necessary to connect the different components, supply containers and samplers.

Four different tubings have been used for the interconnection: the thicker PFA tubing had an o.d. of 3.2 mm and an i.d. of 2.0 mm, whereas the thinner hose had an o.d. of 1.6 mm and an i.d. of 0.75 mm. For the high pressure applications mainly PEEK tubings with an o.d. of 1.6 mm and an i.d. of 0.75 mm were used. For the injection loop and the connection from the injection valve to the safety venting valve a tubing with an i.d. of 1.0 mm offered shorter length with larger storage volume. The wider PEEK tubing avoided flow restrictions and clogging of particles in the samples. For the installed 10 mL injection loop the length was around 12 m instead of almost 23 m when using a tubing with an i.d. of 0.75 mm.

The PFA tubing with 3.2 mm was used for the acid and sample loops as well as the carrier supply lines to the high pressure pump and the two dosing pumps. Additionally, all lines from the carrier tank to the connection block and from the block back to the waste container consisted of the same hose material. The reagents and sample lines as well as all internal rinsing and transfer lines used the smaller 1.6 mm tubing to reduce the dead volume.

The most critical part of the assembly was the installation of six to eight connection tubings on one TitanEX valve. Because of the special sealing technique there were no problems with the simple life time experiments using waste water with only three connections. Nevertheless the high number of tubings needed for the real operation was difficult to install. A fitting-less installation was found to be useful, but the central tube holder (ram) did not manage to fix all tubings with the same strength and tightness. The different forces on the ferrules (see Fig. 8 - 5) caused permanent air leakage for some hoses. The water or reagents in the supply lines fell back to the containers after the start-up due to the leaks. The air in the hoses was then mixed with the other liquids and caused permanent air bubble errors and process breaks.

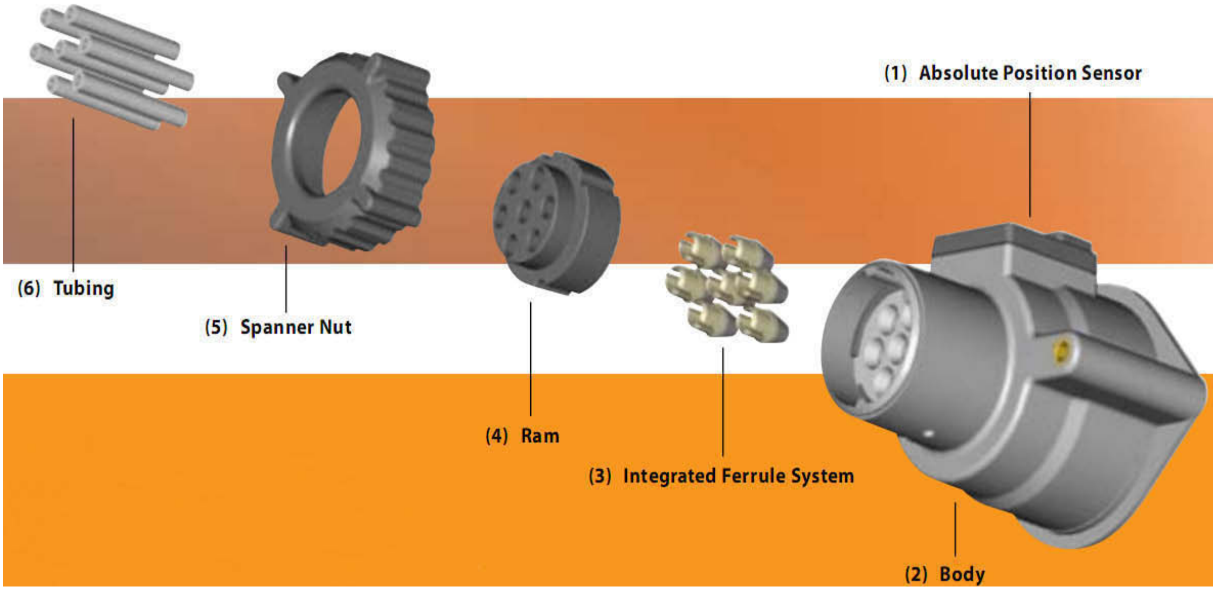


Fig. 8 - 5 The sealing parts of the TitanEX low pressure distribution valve

A temporary solution for that problem was the alternative installation of the tubings. Instead of using the O-Rings in the valve body part for frontal sealing the connection hoses were pushed through the rings to allow axial sealing. This modification allowed permanent and air tight sealing for all connected tubings and therefore a reliable operation. In Fig. 8 - 6 the two different installation methods are shown. For the standard method the tubings were pressed to the O-ring by means of the ferrule. In the new approach the hoses were sealed by means of the axial O-rings.

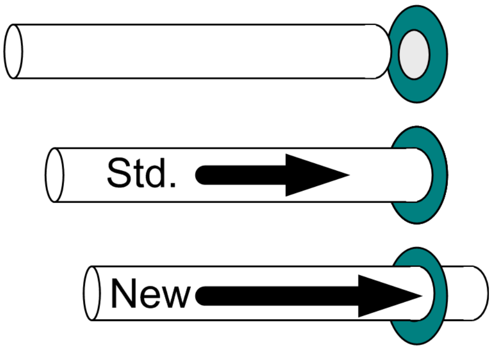


Fig. 8 - 6 Air tight sealing of the PFA hosing due to different installation of the O-Rings

The difficulty was to push the relatively soft hoses through the ferrules and the O-rings. If the PFA hose did not penetrate the O-ring the ferrule deformed the O-rings while the spanner nut was tightened. Without the PFA hose positioned in the center the O-ring was deformed and did not seal properly. For such deformed sealing rings only reopening, replacing and resealing led to a successful installation. The problem was that the wrong installation with subsequent leakage could only be found during the rinsing procedure with detected air leaks.

8.2.2 Test and optimization of the startup routines

The new software allowed automated startup routines from a dry instrument to a status ready to run samples at 300℃ and 150 bar pressure. The startup included the filling of all connection lines, the reactor shaping process as well as heating and pressure buildup.

The successful filling of the supply line was tested via the bubble sensor. By purging the pumped solutions through the bubble sensor into the waste container the system was tested for air in the solution. No air bubbles in the waste line represent complete filling. After all lines were filled without air the high pressure pump started to apply 40 bar in the reactor. The pump stopped and the heating was activated to increase to 220℃. At that temperature the PTFE-TFM liner was softened according to the supplier's recommendation. After the set temperature had been reached, the pump started again, slowly increasing the pressure to more than 100 bar. During that phase the liner was shaped to the supporting tube. After the liner had reached its final size, the reactor heating continued to 300 ℃ while the pump run at 0.2 to 0.5 mL/min to maintain the pressure.

As soon as the system had reached the set digestion temperature, the software allowed to start the first digestion.

For the optimization of the startup routine it was necessary to adjust the pump and purge speed settings to avoid too high or too low pressure in the dosing system. The pressure was measured by a pressure sensor mounted on the sample pump module.
Every time the hose sealing at the valves did not fit properly, as described above, the start-up failed. Permanent air leaks caused time-out errors which indicated wrong sealing of the tubings as the valves permanently supplied the system with solutions containing air bubbles.
To fill the high pressure line for a faster startup routine the safety venting valve port, located between the reactor and the injection valve, was used to purge the pump. By means of a syringe the carrier was drawn into the degasser, the pump and the injection valve (see red line Fig. 8 - 7). The high pressure pump is designed for self priming but due to the relatively long connection tubings from the carrier tank and the degasser, the dry run time is quite long. Manual purging reduces dry run time and mechanical abrasion of the pump significantly.

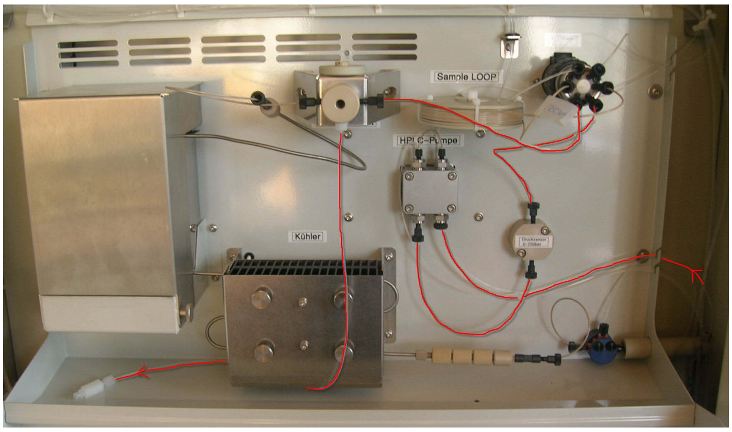


Fig. 8 - 7 Manual purging of the high pressure pump using the safety valve outlet

8.2.3 Testing of normal and alarm shutdown behavior

At the end of usual digestion runs the system should not simply be switched off to avoid possible reactor damages. The main problem is the extreme thermal expansion of the PTFE-TFM tubing material at 300 °C. Compared to the titanium tubing the circumference of PTFE-TFM increases by 20 to 30 % at the set temperature. Normally the material would start to crinkle, but the enormous pressure keeps the liner in shape. In case the internal pressure decreases quickly without cooling the liner would collapse inside the titanium tubing. The formed recess would stress the liner material, therefore reducing the life time of the reactor.

To avoid these problems the system cooled down to 100 °C when the stop button was pressed and only then the pump switched off. Until that temperature the pump set at a minimum pressure of 100 bar keeping the liner in shape.

In case of an emergency stop or a leak in the high pressure system the pressure stabilization feature is not available. Emergency stop tests showed that the new reactor design improved stability in general. The repeated pressure drops after cutting the sample loop did not cause immediate damage of the reactor. The drained condensation liquid or the service time of the reactor did not change drastically, but for normal operation a smooth shutdown is recommended.

8.3 System software tests

Before the real acid application method could be verified, software features and settings needed to be optimized. For that purpose the system was connected to distilled water containers to run acid and sample mixing routines without the risk of contamination and acid spillage. Due to the weak sensitivity of the bubble sensor for distilled water the solutions were replaced by carrier solution as air bubbles could be detected more easily. No concentrated solutions or acids were used during this test period.

8.3.1 Digestion test runs using carrier solution as reagents and sample

The experiments included checks of the reaction control and sample handling with the new soft- and hardware. During optimization the size of the separating air bubbles, the amounts of rinsing solution for the acid and sample loops as well as the pressure and pump speed limits were adjusted.

Another point was the configuration of the bubble sensor settings. The size of detected bubbles depended on the relation of the dosing speed and the trigger level of the sensor. The sensor indicated air or liquid in the tubing using a sensor read-out frequency of 10 ms. If a small bubble is pumped at low speed the number of counted air signals is similar to the counts coming from a large bubble at high pump rates. The working principle is shown in Fig. 8 - 8. To reach a certain sensitivity it was necessary to limit the pump speed, otherwise too small bubbles would not be detected. Having more than 200 µL air in the system the reactor stopped operation due to a serious pressure drop. The bubble sensor and pump speed was adjusted to detect air bubbles with minimum 10 µL to avoid the transport of many small bubbles into the system. Thus process interruptions by too much air in the system could be avoided and even small leaks were reliably detected.

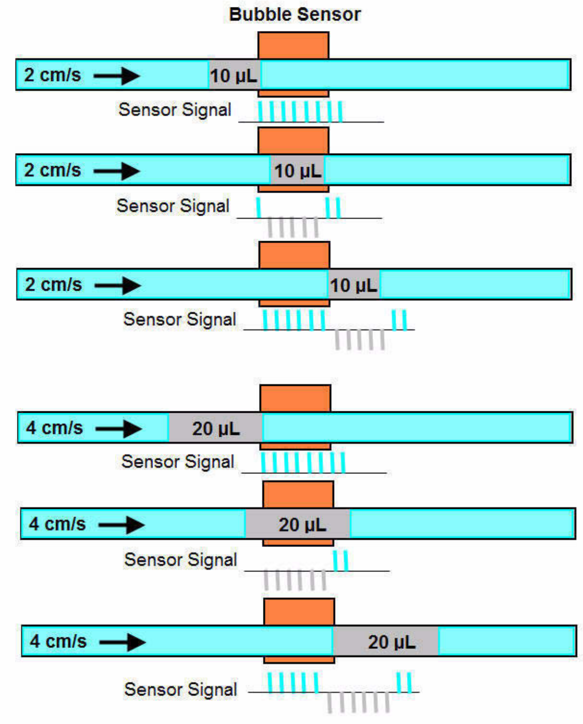


Fig. 8 - 8 Bubble sensor signals as a function of the pump speed

8.3.2 Digestion experiments with autosampler(s)

After successful synchronization and optimization of the digestion and cleaning routines the autosampler needed to be configured.

In a first step the setup was tested with two simple samplers. The advantage of that configuration is the independency of sample input and collection. This fact reduces the need of synchronization to a minimum. The process control was only triggered by the end of the collection time. This was the earliest time to inject the next sample to ensure the collection sampler is back from the rinsing station before the next sample is collected.

In order to run the system with only one autosampler with a dual-probe the synchronization between the sample uptake and the collection needed to be optimized in more detail. While the system collected the last sample the new sample needed to be mixed and injected. This is necessary as the sample-in probe moves together with the collection probe. Both probes are therefore cleaned at the same time in the two rinsing stations before they are moved to the next sample position. That is at the same time the reason why the vessel positions cannot be chosen randomly. With one sampler a sequential approach is necessary.

Running the same method from one to the next sample the preparation time could be easily measured. Knowing the retention and the collection time it was possible to set a start point for acid and sample mixing that exactly fits the injection step. Such a timing allows to set the end of sample mixing to the time of sample injection which is at the same time the starting point of the digestion.
Synchronization could help to keep the time for samples in the injection loop as short as possible. This is very important for samples producing reaction gases. The gases could push a part of the sample out of the loop to the open waste port. Another problem is that the formed bubbles can cause a pressure drop in the reactor after injection.

Experiments with the safety cabin:
When opening the safety cabin the included safety switch immediately deactivated the sampler's power supply. This also happened when the leakage detector underneath the sampler detected acid spillage. To continue the process after vial handling it was necessary to reset and initiate the sampler before continuing with the next samples. For the leakage detector the spillage needed to be removed and the sampler had to be initialized. To allow an alarm feedback a signal line was connected from the sampler box to the controller in the digestion system announcing the interruption of the power supply.

After successful synchronization of the sampler and the digestion units and testing all safety switches the system was ready for sample digestion.

8.4 Optimization to reduce carry over effects

To test the cleaning efficiency of the used rinsing routines the autosampler was loaded with different vials containing concentrated and blank solutions respectively. After digestion the solutions were analyzed by means of an ICP-OES to determine the recovery of the known concentration and the contaminations in the blank samples.

The flow digestion system shown in Fig. 8 - 1 was used to determine the optimum parameters for sample collection.

8.4.1 Recovery tests with standard solutions

For the digestion of 1.5 mL aqueous standard solution best results were achieved when the collection started after 120 seconds and 30 mL were collected. The samples were mixed with 1.0 mL HNO_3 and 0.1 mL Sc as internal standard. The recoveries and their standard deviation are shown in Table 8.1. For Cu, Mn and Pb the recoveries are poor but constant, for the other elements the values are in the range of ±10 %. Due to the dilution factor some element concentrations were close to the LOQ.

Table 8.1: Recoveries for a waste water QC solution

	Recovery [%] ± sd	Conc. [µg/mL]
Al	108 ± 22	2.5
Cd	103 ± 3	2.5
Co	95 ± 2	5.0
Cr	95 ± 3	5.0
Cu	70 ± 1	5.0
Mn	129 ± 1	1.0
Pb	54 ± 1	20.1

In Fig. 8 - 9 the carry over from sample to a subsequent blank run is shown. Double blank vials allowed to check the completeness of the rinsing step.

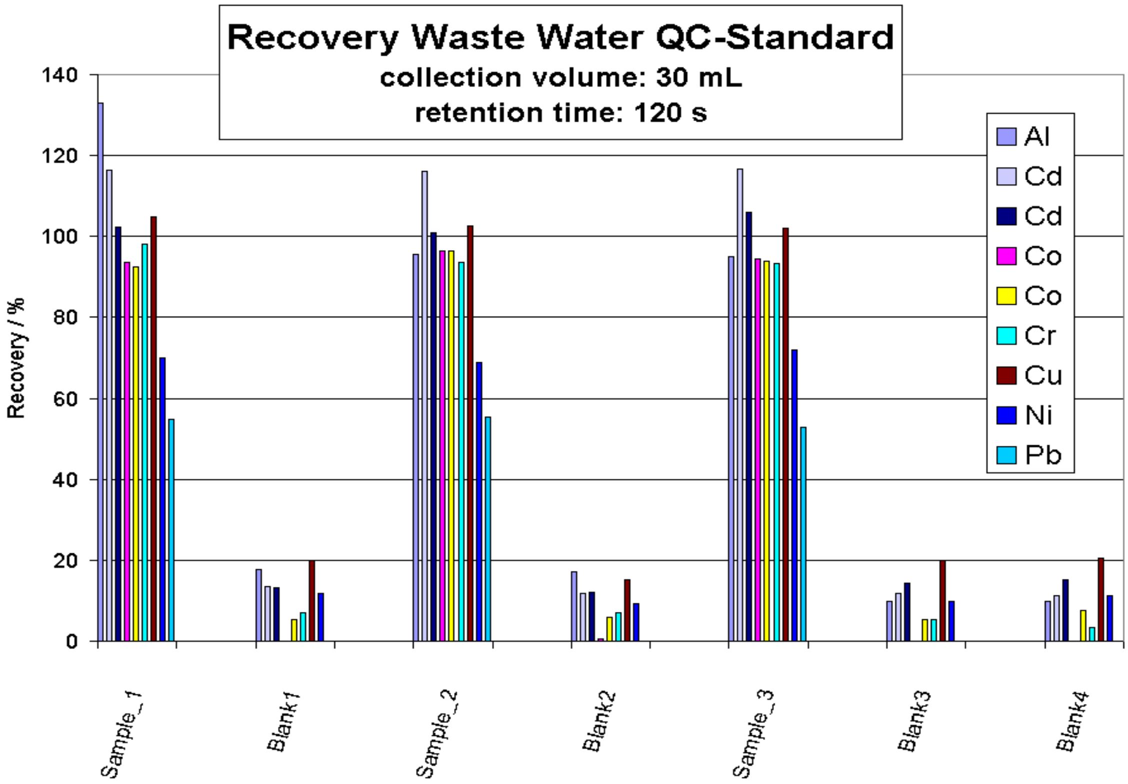


Fig. 8 - 9 Recovery and carry over check for concentrated QC solutions

8.5 Performance verification with waste water and SRM materials

The optimized reaction conditions have been used for experiments with different standard reference materials and waste water. Additionally the waste water samples and an industrial effluent reference material, as well as powdered SRMs were applied after a simple predigestion for homogenization. This procedure was chosen as an alternative to methods described in other works for similar sample materials[14, 26]. There was no need for ultra turrax mixers and due to the good stability of the predigested solutions precipitation could be avoided in the loops and connection lines.

The predigestion took six hours but needed no additional handling except for the transportation of the vials to and from the heating block. The chosen low temperature minimized the risk of losses of volatile elements during this preparation step. The complete process time did not change as the predigestion took place while the flow-system was running the previous batch for high pressure digestion. As soon as the autosampler had finished the last sample the parallel homogenized solutions were entered into the autosampler while the hot block started to prepare the next slurries.

8.5.1 Verification of digestion performance using TOC measurement

To check the digestion efficiency the residual carbon content was measured as totally dissolved organic carbon TOC. For materials with unknown carbon content the TOC value was compared with digestions from a commercial microwave assisted batch system (Multiwave 3000, Anton Paar, Graz, Austria).

Table 8.2 shows the TOC values of the digestion solutions of six different real process waste water samples and one standard reference material. Four of the waste water samples were obtained from a printed circuit board producer containing mainly high iron and copper concentrations as well as some detergents. The fifth sample was a highly polluted mixed raw waste water from a fine chemical producer and the sixth a very low polluted galvanic process waste water. The used SRM lobster hepatopancreas (TORT-2) was applied as slurry after a six hour predigestion at 60°C as described above.

For the flow digestion a sample volume of 2.1 mL was mixed with 0.7 mL HNO_3. The digest was diluted to 15 mL before measurement. The flow system was operated at the optimized conditions with 4 min reaction time at 300°C and a pressure of 160 bar.

In the microwave batch system 20 mL sample was digested with 6 mL HNO_3 and filled up to 50 mL after digestion for the TOC measurement. The microwave batch method consisted of a temperature profile that heated the samples up to 220°C in 15 min and held this level for another 15 min. The maximum controlled pressure with this setting was 40 bar.

Table 8.2: TOC levels for organic samples after microwave batch and flow digestion (n = 4)

Sample	**TOC ± sd [mg/L]**		**Difference [%]**	
	Microwave Oven	Flow System		Note
WasteWater1	40.7 ± 7.2	11.6 ± 2.2	-71	Process waste water samples from PCB-production
WasteWater2	24.9 ± 6.5	12.0 ± 1.6	-52	Process waste water samples from PCB-production
WasteWater3	44.0 ± 11.6	12.8 ± 1.9	-71	Process waste water samples from PCB-production
WasteWater4	26.2 ± 6.3	11.8 ± 0.5	-55	Process waste water samples from PCB-production
Ind.raw Effluent	56.2 ± 10.9	23.7 ± 1.7	-58	Mixed raw waste water from fine chemical production
Ind. Process WasteWater	4.54 ± 0.84	5.69 ± 2.06	25	Galvanic process waste water
TORT-2	162 ± 12	104 ± 9	-36	Lobster Hepatopancreas

The TOC levels after flow digestion are significantly lower compared to the results after microwave digestion except for the very low polluted galvanic waste water.

The absolute digestion efficiency is measured as percent of remaining carbon content which was calculated based on the known carbon content before digestion. In Table 8.3 the results are shown for glucose, glycine, nicotinic acid and SRM TORT-2. As previously described[26], nicotinic acid is very resistant against oxidation with nitric acid. Even with a substantially longer digestion time in the flow reactor it was not possible to attack the compound. In addition to the standard reaction time of 4 min (flow rate 2.5 mL/min) the increase to 6:40 min (flow rate 1.5 mL/min) did not change the result for nicotinic acid. Glucose and glycine however, where decomposed properly within the short time of 4 min inside the hot reactor.

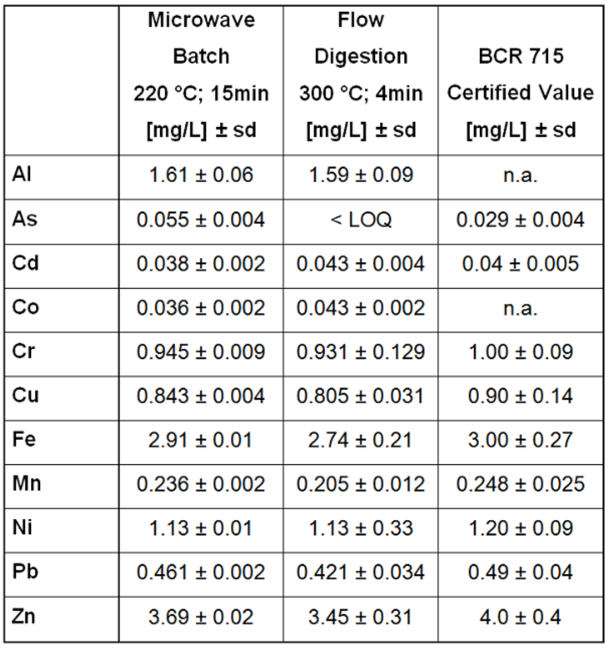
Table 8.3: TOC levels after decomposition of test materials and a SRM (n=3)

Sample	**TOC**	**Flow rate**
	% ± SD	mL/min
Glucose c = 9.1 g/L	4.3 ± 1.4	2.5
Glycine c = 9.0 g/L	5.3 ± 0.4	2.5
Nicotinic acid c = 10.0 g/L	109 ± 14 104 ± 15	2.5 1.5
TORT-2 Lobster c = 9.0 g/L	1.21 ± 0.03	2.5

8.5.2 Trace element determination in waste water samples

An industrial effluent reference material (BCR 715) was analyzed with a Ciros Vision ICP-OES after microwave batch and a high performance flow digestion. For both samples the same procedures were applied mentioned in chapter 8.5.1. For the FDS one sampler with two probes and the sample mixer was used.

Table 8.4: Recovery for BCR 715 Industrial Effluent using microwave or flow digestion (n=4)



	Microwave Batch 220 °C; 15min [mg/L] ± sd	**Flow Digestion 300 °C; 4min [mg/L] ± sd**	**BCR 715 Certified Value [mg/L] ± sd**
Al	1.61 ± 0.06	1.59 ± 0.09	n.a.
As	0.055 ± 0.004	< LOQ	0.029 ± 0.004
Cd	0.038 ± 0.002	0.043 ± 0.004	0.04 ± 0.005
Co	0.036 ± 0.002	0.043 ± 0.002	n.a.
Cr	0.945 ± 0.009	0.931 ± 0.129	1.00 ± 0.09
Cu	0.843 ± 0.004	0.805 ± 0.031	0.90 ± 0.14
Fe	2.91 ± 0.01	2.74 ± 0.21	3.00 ± 0.27
Mn	0.236 ± 0.002	0.205 ± 0.012	0.248 ± 0.025
Ni	1.13 ± 0.01	1.13 ± 0.33	1.20 ± 0.09
Pb	0.461 ± 0.002	0.421 ± 0.034	0.49 ± 0.04
Zn	3.69 ± 0.02	3.45 ± 0.31	4.0 ± 0.4

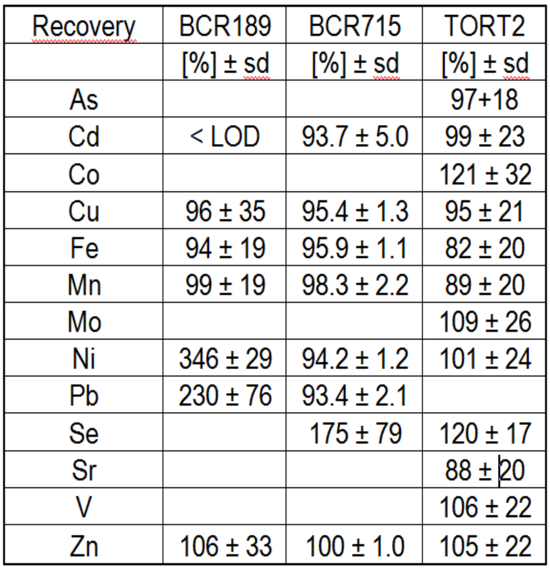
Both digestion systems gave results within the certified range of the reference material (Table 8.4). The standard deviations for the microwave digestion system were smaller compared to the FDS. The reason for this was most likely the higher element concentration in the digests because of the lower dilution factors of the solutions from the microwave batch system compared to the FDS. The handling time necessary for four samples and the blank was at least 25 minutes. This time included only sample weighing, acid addition, dilution, container handling and cleaning. The needed time for microwave digestion and cooling, in sum 45 minutes, was not included. Overall, the waste water needed 1 hour and 10 minutes in the microwave system for five samples. In the flow system the same number of samples needed only 30 min (five times 6 minutes). Manual handling was limited to filling approximately 5 mL sample solution in the vials and placing them into the autosampler together with 5 empty collection vials. Together with loading the sample list in the software the labour time needed was less than 5 minutes including documentation. This drastic reduction of handling time and costs compensates in most cases the lower quality of the final results.

8.5.3 Trace element determination in slurry samples

The analytical results for the solid SRM-slurries are shown in Table 8.5. An amount of 2 g sample each was mixed in 50 mL vials with 25 mL concentrated nitric acid and heated on a graphite heating block for 6 hours at 60℃. The predigestion resulted in dark colored and turbid solutions not applicable for direct measurement, but these solutions were stable enough to be transferred homogeneously into the automated digestion system.

For every sample 4 mL of the pretreated slurry were digested at 300℃ and 160 bar with a flow rate of 2.5 mL. The digests were collected and diluted to a final volume of 30 mL. The analysis of the samples was carried out with a single robust ICP-OES method. This approach was selected to show that this combined analytical technique can be applied to a variety of sample materials and elements without the interaction of the operator and the optimization of measurement.

Table 8.5: Recoveries for solid reference materials after flow digestion using predigested slurries (n=4)



Recovery	BCR189	BCR715	TORT2
	[%] ± sd	[%] ± sd	[%] ± sd
As			97+18
Cd	< LOD	93.7 ± 5.0	99 ± 23
Co			121 ± 32
Cu	96 ± 35	95.4 ± 1.3	95 ± 21
Fe	94 ± 19	95.9 ± 1.1	82 ± 20
Mn	99 ± 19	98.3 ± 2.2	89 ± 20
Mo			109 ± 26
Ni	346 ± 29	94.2 ± 1.2	101 ± 24
Pb	230 ± 76	93.4 ± 2.1	
Se		175 ± 79	120 ± 17
Sr			88 ± 20
V			106 ± 22
Zn	106 ± 33	100 ± 1.0	105 ± 22

The recoveries for most elements are within the range of ±10 % and some of them are within ±20 %. Only very low concentration of Ni and Pb in the whole meal flour (BCR 189) and Se in wastewater (BCR 715) gave bad results.

8.6 Technical drawbacks and difficulties

The initial good analytical results for the waste water samples and the slurries did not compensate for the recurring technical problems. In addition to repeated acid drops from the sample valve, broken sample loops and deformed backpressure seals the system experiments were interrupted repeatedly. It was not possible to operate the instrument continuously for two weeks. There were frequent mechanical failures which required the operator's interaction.

8.6.1 Leakage due to pressure peaks

The 10 port distribution valves used for the sample and acid mixture lost approximately 0.5 to 1.0 mL via their drain holes every day. The reason for the loss were partly leaks coming from poorly sealed tubings or losses from the sealing disc. These losses were caused by pressure peaks from the injection valve. The injection loop on the injection valve had a volume of 10 mL. Due to the enormous pressure in the high pressure system the loop tubing (PEEK with o.d. of 1.6 mm and an i.d. of 1.0 mm) expanded when switched to the injection position. This elastic deformation increased the volume of the loop. After the injection valve switched back to the load position the described expanded volume was responsible for producing a sharp pressure peak against the acid and sample valves and the waste port of the injection valve respectively. The open ended waste line caused a remarkable resistance due to its length, therefore the pressure peak also hit the sealing discs of the two TitanEx valves. As both were connected to the injection valve via the mixing-T the shock wave pressed out a few µL from the drain port with every switching action (see Fig. 8 - 10).

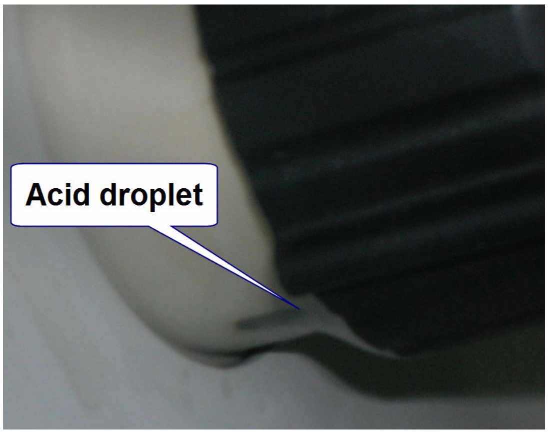


Fig. 8 - 10 Acid droplet on the acid valve drain port

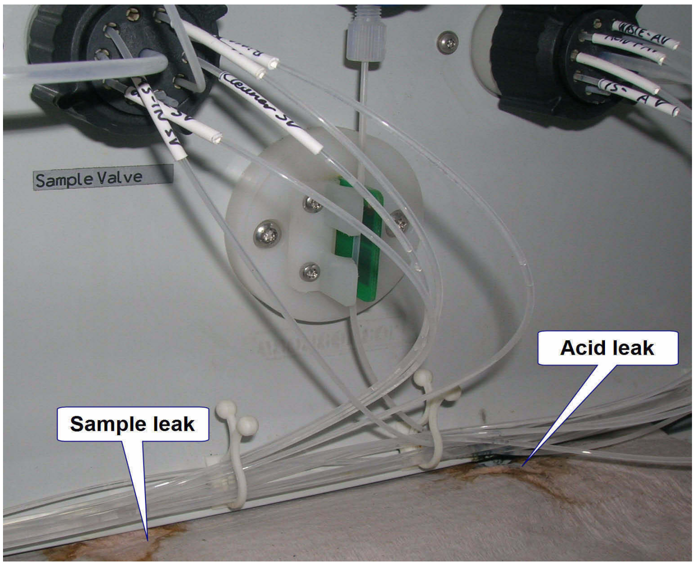


Fig. 8 - 11 Leakage indication with paper underneath the valves as indicator

This behavior was not found during the service time experiments as the injection valve and injection loop were missing in the setup. The few µL did not cause analytical problems, but the acid drops attacked the coating of the instrument leaving yellow and brown spots after only one or two weeks of operation. On one instrument the coating was completely destroyed leaving the blank sheet steel behind.

In addition to the easy detectable visual coating corrosion a more critical point for the function was the acid attack inside the valve handling the acids. The concentrated acids, pressed out from the wetted parts made of PTFE, attacked the casing materials. These materials were not resistant against nitric acid and were damaged as a result. Fig. 8 - 12 and Fig. 8 - 13 show the disassembled valve with strong corrosion. The PEEK materials were attacked after maximum two to three weeks of operation due to permanent nitric acid losses. Metal components such as the wire spring holding the stator or the disc spring package behind the rotor were corroded by hydrochloric acid.

The leakage could be partly fixed by using modified O-Rings. The green colored O-Rings were replaced by black colored chemically inert viton O-rings. Another improvement was the installation of the O-Rings on the tubing as shown in chapter 8.2.1. The installation of these O-rings was very difficult due to the high number of ports and the relatively short tubings. The length was limited to reduce unnecessary dead volumes in the system.

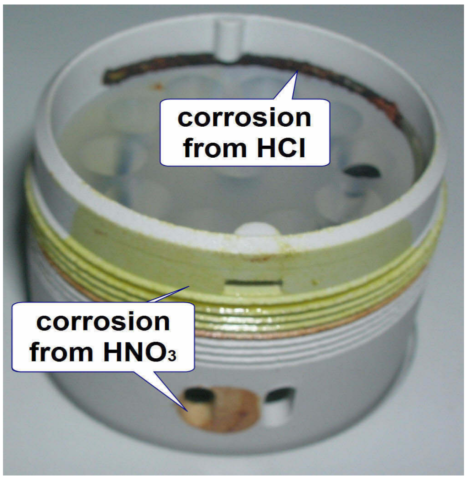


Fig. 8 - 12 Acid attack on the TitanEx valve plastic body and metal spring after 2 weeks of operation

Fig. 8 - 13 Corrosion caused by HCl on the spring package holding the rotor sealing disk

The pressure peaks from the system, which were the main reason for the difficulties, could not be eliminated. Possible solutions like a check valve or restrictor capillary between the mixing tubing and the injection valve were outweighed by their disadvantages. The check valve and a thin capillary would not allow the application of particles in the solution. The capillary would also avoid fast loading of the PEEK injection loop as the PVM pumps would not manage to build up enough high pressure to force the sample through the restriction. The check valve would furthermore increase the risk of cross contaminations as the valve ball and valve body could trap sample particles. That is why none of the possible options was realized. Once the system was properly sealed the droplet rate was drastically reduced, but it took quite long to reseal the tubings after a service on the valves.

8.6.2 High pressure PEEK tubing failure

In addition to the slow acid leakage on the low pressure valves another new effect caused permanent interruptions of the test sequences. A new lot of PEEK tubing, used as injection loop on the high pressure 6-port valve, did not reach the service time the first production batch was able to deliver.

For the experiments in the container a coil with 100 m PEEK tubing was used, having an o.d. of 1.6 mm with an i.d. of 1 mm. One sample loop had a length of approximately 12 m to offer a volume of 10 mL. This volume was chosen to allow maximum amounts of acid and sample with two 5 mL pumps. From this PEEK material loops were made and used many weeks in the first prototype configuration. Only repeated air injections caused hot vapor attacks from the reactor and decreased the service time. For the three pilot production units a new PEEK tubing was ordered as only old material for one coil was left. The injection loops for the other units were made from new tubing material delivered by the same producer with the same dimension but from a different production lot. During the experiments the new tubing did not withstand the reaction conditions longer than two weeks in average.

The following failures were detected:

- Broken capillary inside one of the standard super flangeless fittings
- Burst connection tubing between the injection valve and the safety release valve
- Burst connection tubing between the reactor outlet and the backpressure regulator

To find out the difference between the new and the old capillary they were tested separately. During closer inspection with a microscope and mechanical tests the following different characteristics could be found:

- **the new material was more brittle causing fractures inside the fittings**

The capillary broke on constriction points on which the fitting pressed into the tubing for mechanical fixation. A similar tubing failure was detected three times. A small part of the broken tubing remained in the fitting (see Fig. 8 - 14). The constriction of an undamaged tubing can be seen in Fig. 8 - 15. The breakage happened at the same position on the other tubing, but no stress crack can be seen on the position.

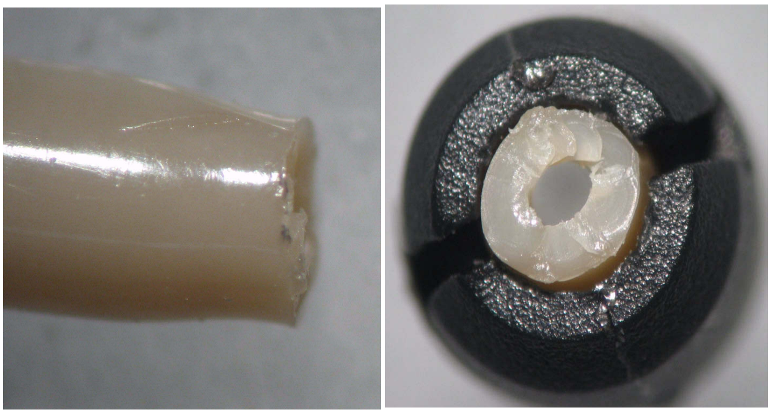


Fig. 8 - 14 End of a broken capillary and its remaining part inside the fitting

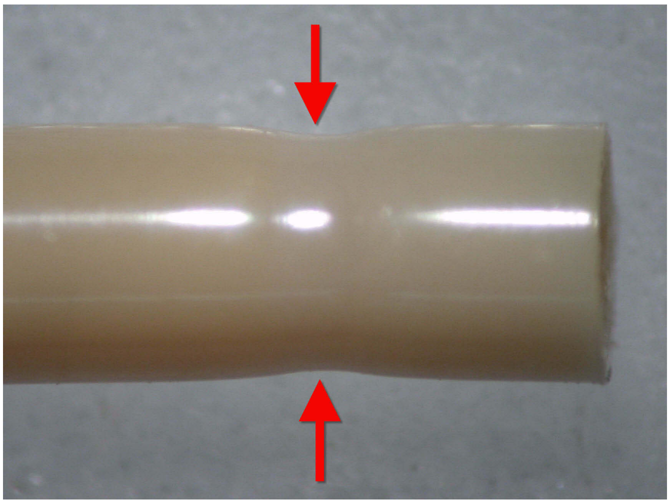


Fig. 8 - 15 Used but undamaged tubing showing the constriction of the fitting

- **the new tubing was not properly produced concerning constant wall thickness**

During the installation of the new PEEK tubing variations in wall thickness were detected. In Fig. 8 - 16 a cross-sectional area with varying dimensions can be seen. These variations are probably the reason for tubing failures which have been seen beside the breakage inside the fittings. Fig. 8 - 17 shows a longitudinal crack after a tubing failure and another position of the same tubing shows signs of further cracks under the microscope (Fig. 8 - 18).

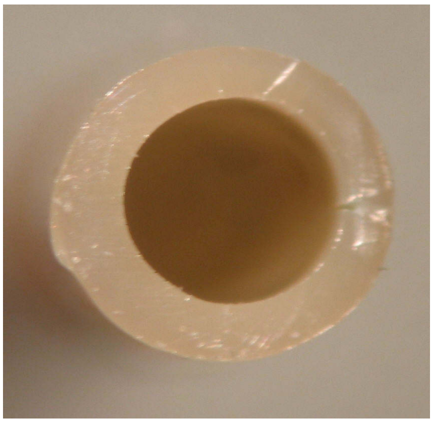


Fig. 8 - 16 Wall thickness variations of the new PEEK tubing

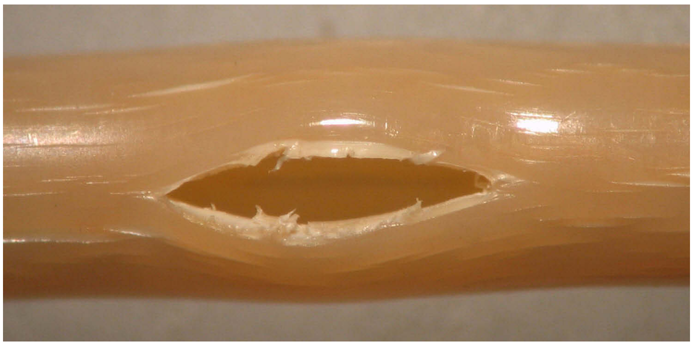


Fig. 8 - 17   Longitudinal hole in a new PEEK tubing after 12 days of operation

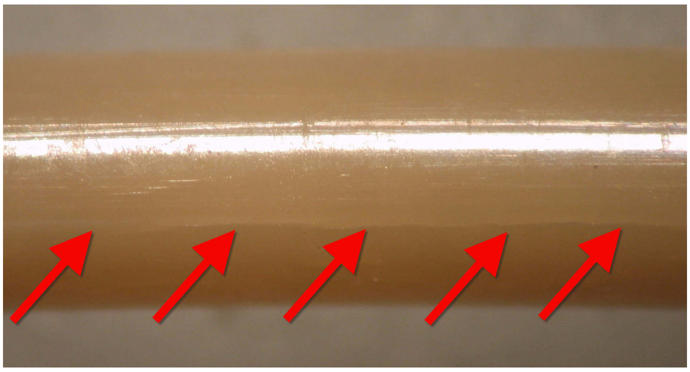


Fig. 8 - 18   Longitudinal crack on a different position of the new PEEK tubing after 12 days of operation

- **the new tubing material was more sensitive to small bending radii**

The new material’s sensitivity to bending radii was compared to the sensitivity of the old material. Short pieces of tubing were bent 45° and inspected with a microscope after the experiment. The tubing was fixed in a block with a fitting hole for the experiment. The detailed setup is shown in Fig. 8 - 19, the resulting damages can be seen in Fig. 8 - 20 and Fig. 8 - 21.

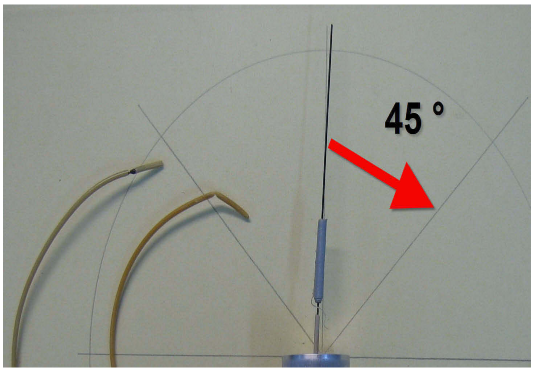


Fig. 8 - 19 Bending test setup for PEEK capillaries

Fig. 8 - 20 Not broken used capillary made from the previous material after the bending test

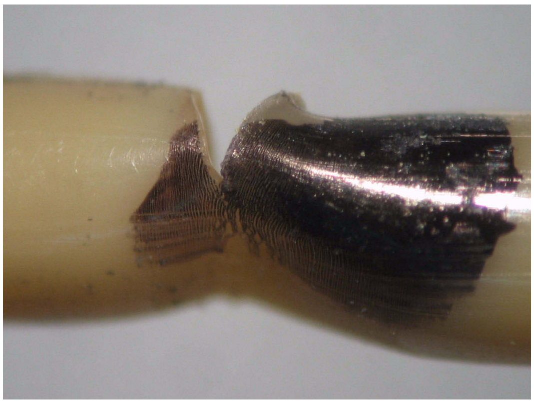


Fig. 8 - 21 The new capillary material with black marking at the breaking point

As can be seen in the microscope pictures the bad corroded old tubing material creased, but did not break. The sample tubing was taken from an injection loop which had been used a long time before. In contrary the new but brittle material broke before it creased.

The producer of the tubing material recommended to anneal the material before use, especially after shaping the loop in a relatively small radius. The result of the heating process was a coil that kept its shape without fixing it. The lost tension was obvious, but did not improve the service time of the tubing. The maximum service time for the loop installed in the high pressure line was still no longer than two weeks.

Increasing the wall thickness of the tubing could give additional safety against breakage, but would at the same time increase the tubing length and therefore the flow resistance for the filling process. The reduction of the inner diameter from 1.0 mm to 0.75 mm would, for example, increase the loop length from 12 to 23 meter!

The application of a lined tubing was also discussed but rejected. The liner would shrink and expand for every injection step. This constriction would drastically increase the pressure peak effect which has already been observed for the normal PEEK tubing. Even more critical for the operation would be the pressure drop resulting from the filling of the gap between the liner and the supporting tubing.

These drawbacks and missing options were the reason why the performance experiments were done with sample loops which were replaced every 14 days.

8.6.3 Backpressure valve failure

The backpressure regulating material, used in the standard version, was a Viton disc as flexible sealing element. To increase the chemical resistance against the used acids all regulators were modified by a Kalrez disc with an additional PFA protection coating. The valves typically lasted three months during the test phase and could be refurbished with a new sealing disc. The end of lifetime of a sealing disc was indicated by an increase of the pressure hysteresis between low and high flow rates. Normally the variation was maximum 15 to 20 bar for flow rate changes and between 0.5 and 2.5 mL/min for a new seal. At the end of the service time variations of up to 50 bar could be observed.

During the experiments the system stopped several times as 90 to 100 bar could not be exceeded at system startup. The reason was a deformed or damaged Kalrez discs releasing the pressure too early. Later on it was discovered that the problem was a clogged check valve on the high pressure pump which stopped operation at the pressure mentioned. As the pressure did not increase the backpressure valve was closed more and more to increase the pressure, but this measure damaged the sealing discs.

The deformed discs are shown in Fig. 8 - 22 indicating too strong closing of the valve which furthermore caused the damage. In the right-hand side of the figure the thin release hole in the valve can be seen.

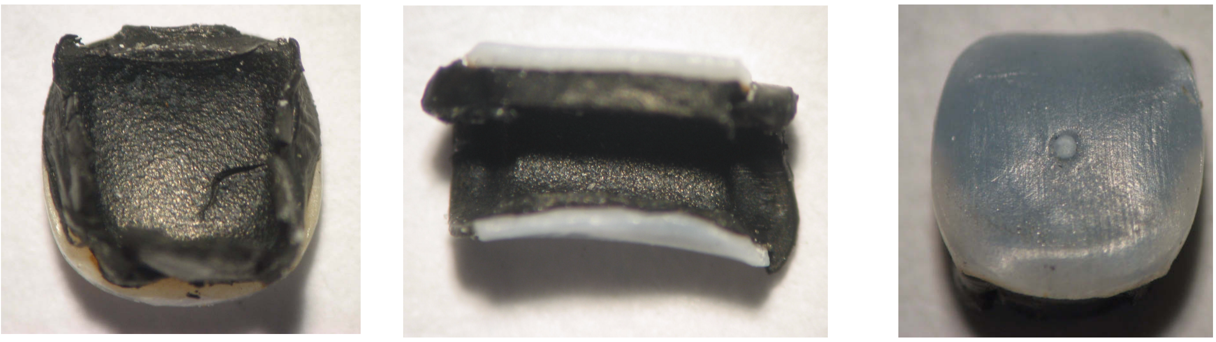


Fig. 8 - 22 Damaged sealing discs made of Kalrez for the backpressure regulator

8.7 Conclusion

In this section the application's performance as well as the technical drawbacks were discussed. Even though the performance of the experiments showed the advantages of such an automated approach the number of problems did not allow to operate the instruments with the needed reliability. For a continuous operation of 7 days a week and 24 hours a day the operation performance was not robust enough. Running three independent systems in parallel, which showed the same errors, indicated the weak points in the design.

The problem with the dripping valves could not be improved without completely changing the setup again as the error occurred due to the valve design. This would mean running the soft- and hardware optimizations again with other types of valves, ideally using the Vici valves. The change would not only increase the development costs but also the costs for a single instrument. The valves are needed at least three times in the setup and they are three times more expensive. Before experiments with the alternative valves were conducted it was not possible to determine whether a similar design with a rotating sealing disc would show similar leakage effects compared to the TitanEx valves or not.

A similar uncertainty resulted from the PEEK tubing. Only the change of the production lot drastically reduced the performance of the material. Such parameters are inacceptable for a serial production asking for long time service support and constant performance.

In addition to the technical problems the waste water monitoring project, giving the initial impulse for the project, was cancelled as well. The risk of losing the additional money for further development was too high to continue. The market size for such automated system is small, partly because of the high price of the configuration. Due to market concentration for waste water laboratories in European countries and the USA the total number of laboratories decreased. There are less than 100 laboratories needing sample preparation for waste water samples at such high numbers. These low numbers limit the possibility to divide the additional costs for further improvements. This fact increases the sales price while reducing the chance to sell higher numbers.

The sum of technical and marketing difficulties was responsible for the termination of the project. The robust parts of the configuration such as the reactor, the injection valve and the high pressure pump may be used for other online applications in the future. The firmware and electronic boards were operated without troubles and errors as well. These parts could find their ways into a flow synthesis system or a nitrogen and phosphorous combustion unit for wastewater analysis. Important for all future configurations is the need to reduce the complexity of the liquid handling around the reactor. This would help to avoid errors and increase the operation stability. It is only a question of time until the unique features of the reactor tubing may find their perfect field of application. The task is to profit from the advantages and the performance while at the same time avoid the obstacles.

9 Literature

1 L.T. Skeggs Jr., Clin. Chem. **2** (1956) 241-250

2 L.T. Skeggs Jr., Amer.J. Clin. Pathol. **28** (1957) 311-322

3 J. Lacy, Analyst **90** (1965) 65-75

4 J.R.Sarbeck, P.A. St John, J.D. Winefordner, Mikrochim. Acta **149** (1972) 55-64

5 F.S.Chuang, J.R Sarbeck, P.A. St John, J.D. Winefordner, Mikrochim. Acta **187** (1973) 523-531

6 J. Ruzicka, E.H.Hansen, Anal. Chim. Acta, 78 (1975) 145-157

7 M. Burguera, J.L. Burguera, *Anal. Chim. Acta*, **179** (1986) 351-357

8 M. Burguera, J.L. Burguera, *Anal. Chim. Acta*, **214** (1988) 421-427

9 S. Hinkamp, G. Schwedt, *Anal. Chim. Acta* **236** (1990) 345-350

10 R.L. Benson, I.D. McKelvie, B.T. Hart, I.C. Hamilton, *Anal. Chim. Acta* **291** (1994) 233-242

11 V. Carbonell, M. de la Guardia, A. Salvador, J.L. Burguera, M. Burguera, *Anal. Chim. Acta* **238** (1990) 417-421

12 M. Burguera, J.L. Burguera, *JAAS* **8** (1993) 235-242

13 J.L. Burguera, M. Burguera, M.R. Brunetto, *Atomic Spectros.* **14** (1993)

14 M. Burguera, J.L. Burguera, C. Rondon, C. Rivas, P. Carrero, M. Gallignani, M.R. Brunetto, *JAAS* **10** (1995) 343-347

15 S.J. Haswell, D. Barclay, *Analyst*, **117**, 117, 1992

16 D.L. Tsalev, M. Sperling, B. Welz, *Analyst* **117** (1992) 1729-1733

17 B. Welz, D.L. Tsalev, M. Sperling, Anal. Chim. Acta, **261**, 91, 1992

18 T. Guo, J. Baasner, *Talanta*, **40**, 12, 1927,1993

19 C.P. Hanna, S.A. McIntosh, *Atomic Spectros.* **16** (1995) 106-114

20 A. Morales-Rubio, M.L. Mena, C.W. McLeod, *Anal. Chim. Acta* **308** (1995) 364-370

21 C.C. Huang, M.H. Yang, *Anal. Chem.* **69** (1997) 3930-3939

22 J.L. Burguera, M. Burguera, P. Carrero, M.R. Brunetto, *Anal. Chim. Acta*, **308** (1995) 349-354

23 L.J Martines Steward, R.M. Barnes, *Analyst*, **119** (1994) 1003-1010

24 B. Welz, Y. He, M. Sperling, *Talanta* **40** (1993) 1917-1926

25 G. Knapp, *Fresenius Z. Anal. Chem.*, **317** (1984) 213-219

26 U. Pichler, A. Haase, G. Knapp, *Anal. Chem.* **71** (1999) 4050-4055

27 T.J. Gluodenis, J.F.Tyson, *JAAS* **7** (1992) 301-306

28 T.J. Gluodenis, J.F.Tyson, *JAAS* **8** (1993) 697-704

29 H. Berndt, J. Yanez, JAAS **11** (1996) 703-712

30 C.J. Mason, G. Coe, M. Edwards, P. Riby, *Analyst* **125** (2000) 1875-1883

31 V. Karanassios, F.H. Li, B. Liu, E.D.Salin, *JAAS* **6** (1991) 457-463

32 S. Haiber, H. Berndt, *Fresen. J. Anal. Chem.* **368** (2000) 52-58

33 C. Gräber, H. Berndt, *JAAS*, **14** (1999) 683-691

34 P. Jakob, H. Berndt, *JAAS* **17** (2002) 1615-1620

35 M. Würfels, E. Jackwerth, *Fresenius Z. Anal. Chem.* **322** (1985) 345-358

36 M. Würfels, E. Jackwerth, M. Stoeppler, *Fresenius Z. Anal. Chem.* **329** (1987) 459-461

37 M. Würfels, M. Stoeppler, *Fresenius Z. Anal. Chem.* **330** (1988) 159-164

38 M. Würfels, E. Jackwerth, *Anal. Chim. Acta,* **226** (1989) 1-41

39 P. Schramel, L.-Q. Xu, G. Knapp, M. Michaelis, Mikrochim. Acta **106** (1992), 191-201

40 Fili, Oliveira, Oliveira, J. Braz. Chem. Soc., 14 (2003) 435-441

41 Upchurch Scientific Catalog 2007/2008

42 U.Pichler, PH. D. thesis, Weiterentwicklung eines mikrowelleninduzierten Durchflussaufschlusssystems für Aufschlüsse bei hohen Temperaturen, Universtiy of Technology Graz, 1999

43 M.D. De Almeida, K.C. Leandro, C.V. Da Costa, R.E. Santelli, M. La Guardia, *JAAS* **12** (1997) 1235-1238

44 P. D. Tzanavaras, D. G. Themelis, *Talanta* **59** (2003) 207-213

45 J.L. Burguera, M. Burguera, C. Rivas, C. Rondon, P. Carrero, M. Gallignani, Talanta **48** (1999) 885-893

46 S. Gang, C. Xingguo, Z. Yunkun, L. Mancanga, H. Zhide, *Anal. Chim. Acta*, 420 (2000) 123–131

10 Appendix

10.1 Abbreviations and trade names

CFA	continuos flow analysis
CRM	certified standard reference materials
CV-AFS	cold vapor atomic fluorescence spectroscopy
ETV-AAS	electrothermal vaporisation - atomic absorption spectroscopy
F-AAS	flame - atomic absorption spectroscopy
FIA	flow injection analysis
FIMS	flow injection mercury system
GUI	graphical user interface
HPLC	high performance liquid chromatography
HT-HHPN	high temperature hydraulic high pressure nebulization
ICP-OES	inductively coupled plasma optical emission spectrometry
Kalrez	trademark DuPont, perfluoro elastomer
Kel-F	trademark 3M, PCTFE polychlortrifluorethylene
NBS	national bureau of standards
PEEK	polyetheretherketone
PPVE	perfluoropropylene vinyl ether
PTFE	polytetrafluorethylene
PTFE-TFM	copolymer of PTFE and PPVE (< 0.1%)
RS-232	standardized serial data communication interface
SRM	standard reference materials
TOC	total organic carbon
ULTEM	trademark General Electric, polyetherimid PEI
Viton	trademark DuPont, fluoro elastomer

10.2 List of figures

10.3 List of tables