Doctoral Dissertation

DEVELOPMENT OF A NOVEL METHOD AND INSTRUMENTATION FOR THE ANALYSIS OF VOLATILE ORGANIC SUBSTANCES BY ICP-OES

A Dissertation Presented

By

FARZANEH MORADI

Supervisors

Em.Univ.-Prof. Dipl.-Ing. Dr.techn. Günter Knapp

Dipl.-Ing. Dr.techn. Helmar Wiltsche

Institute of Analytical Chemistry and Food Chemistry

Graz University of Technology

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To Professor Dr. Günter Knapp

for his invaluable guidance and support

STATUTORY DECLARATION

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.

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Approved as to style and content by:

Em.Univ.-Prof. Dipl.-Ing. Dr.techn. Günter Knapp
Institute of Analytical Chemistry and Food Chemistry
Chairperson of Committee

Dipl.-Ing. Dr.techn. Helmar Wiltsche
Institute of Analytical Chemistry and Food Chemistry
Member

Ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Karl Gatterer
Institute of Physical and Theoretical Chemistry
Member

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ABSTRACT

The goal of this dissertation work was the development of a novel method and instrumentation for the determination of metals in volatile organic solvents by means of ICP-OES. As the inductively coupled plasma can be strongly interfered by higher amounts of organic compounds the removal of the organic part of the sample is therefore a demand. The method and instrumentation of this work consist of two parts. The first part deals with the combustion of the nebulized sample solution where the carbon of the organic compounds is converted to CO_2. For this purpose a combustion oven from a commercial carbon analyzer was used. The second part is the removal of CO_2 and remaining oxygen as complete as possible. Three equipments have been investigated, a falling film column, a hollow fiber gas exchanger and a PTFE membrane desolvator. The proposed combustion/carbon removal approach allowed stable operation of the ICP even when introducing highly volatile solvents such as dichloromethane or acetone that otherwise would have immediately extinguished the plasma. Analyte signals in halogenated solvents were found to be significantly higher than in non-halogenated ones and non-linear calibration functions were observed for all investigated analytes below 5 mg kg^{-1}. Though a stable operation of the plasma was possible, the analyte signal intensities obtained in water were, depending on the element and the solvent, between 1.5 and 2800 times higher than in halogenated solvents.

As small amounts of CO_2 may pass the removal section, the influence of this gas on the plasma conditions was investigated. In this aim, CO_2 was artificially added to the nebulizer gas flow and the effect of CO_2 on signal intensity of various elements and plasma robustness was determined. Our results confirmed literature reports that the presence of CO_2 induces a signal enhancement for elements with ionization potentials higher than 9 eV such as As, Se and Zn. For these elements an increase in signal intensity of up to a factor of 2 was observed at 1.6 % v/v CO_2 added to the nebulizer gas flow, while a decreasing was encountered with further increasing of the CO_2 concentration. For elements with ionization potentials lower than 9 eV the signal intensity decreased with increasing CO_2 concentration in the nebulizer gas flow. Moreover, the plasma robustness expressed as the Mg (II) $_{280.2,\ nm}$/Mg (I) $_{285.2,\ nm}$ ratio first increased when the CO_2 concentration in the nebulizer gas flow was increased and then decreased linearly.

As the enhancement or suppression of analyte signal is strongly dependent on the CO_2 concentration present, it is important that the CO_2 concentration remains at a constant level during calibration and subsequent analysis of the sample. Therefore, the solvent used for preparing the calibration should match the solvent in the sample. Though this requirement is also a standard procedure for the analysis of aqueous samples (acid matching), it impedes the analysis of samples of unknown organic composition.

KURZFASSUNG

Das Ziel dieser Arbeit war die Entwicklung von neuen Methoden und Geräten zur Bestimmung von Metallen in flüchtigen organischen Lösungsmitteln durch Plasmaemissionsspektrometrie. Da die Einbringung größerer Mengen Kohlenstoff das ICP destabilisiert, muss dieser vor dem Plasma entfernt werden. Der experimentelle Teil der vorliegende Arbeit ist in zwei Teile gegliedert: Im ersten Abschnitt wird die Verbrennung der zerstäubten Probe in einem kommerziell erhältlichen Verbrennungsofen eines C-Elementaranalysators in einer sauerstoffreichen Atmosphäre diskutiert. Im Ofen wurden die Kohlenstoffspezies der Probe zu CO_2 umgesetzt. Im zweiten Abschnitt wird die Abtrennung von Kohlendioxids und Sauerstoffresten diskutiert. Eine mit wässriger Natronlauge beschickte Fallfilmabsorberkolonne, ein Hohlfaserbündelaustauscher und ein PTFE-Membrandesolvator wurden dahingehend untersucht. Die Kombination aus Verbrennung des Lösungsmittels mit der nachfolgenden Abtrennung von CO_2 und Restsauerstoff ermöglichte einen, vom eingebrachten Lösungsmittel unabhängigen, stabilen Betrieb des Plasmas. Die Emisssionssignale von Analyten in halogenierten Lösungsmitteln waren signifikant höher als nichthalogenierten, jedoch waren diese um 1,5 bis 2800 mal kleiner als in Wasser. Unabhängig von der untersuchten Probe wurden gekrümmte Kalibrationsfunktionen erhalten, wenn die Analytkonzentration unter 5 mg kg^{-1} lag.

Da die Abtrennung von CO_2 im Membrandesolvator nie vollständig sein kann, wurde der Einfluss geringer Mengen von CO_2 auf die Intensität verschiedener Emissionslinien bzw. auf die Robustheit des Plasmas untersucht. Die Ergebnisse bestätigen das literaturbekannte Faktum, dass die Anwesenheit von CO_2 im ICP die Emissionsintensität von Elementen mit einem Ionisationspotential von über 9 eV verstärkt. Für As, Se oder Zn wurden, je nach beobachteter Emissionsline, eine Intensitätsverdopplung beobachtet, wenn 1,6 % v/v CO_2 zum Zerstäubergasstrom zugesetzt wurden. Bei Elementen mit einem Ionistationspotential von kleiner als 9 eV wurde mit steigender CO_2-Konzentration sinkende Eimissionsintensität beobachtet. Mit steigender CO_2-Konzentration im Zerstäubergasstrom stieg auch die Plasmarobustheit (Mg (II) $_{280.2,\,nm}$/Mg (I) $_{285.2,\,nm}$) zuerst am und fiel dann aber nahezu linear ab.

Da die Emissionsintensität der Analyten stark von der CO_2-Konzentration im ICP abhängt, ist es wichtig diese während der Kalibration und Probenmessung konstant zu halten.

Daher sollte das in der Probe enthaltene Lösungsmittel auch zur Herstellung der Kalibrationsstandards genutzt werden. Dies entspricht der, auch bei der Analyse von wässrigen Proben häufig genutzten Technik des „Säure-Matchings“. Andererseits behindert diese Anforderung die Analyse unbekannter Lösungsmittel.

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Part 1

INTRODUCTION

1.1 Dissertation objectives and rationale

The goal of this dissertation was to develop a novel method and instrumentation for the introduction of organic solvents to inductively coupled plasma optical emission spectrometry (ICP-OES). In this regard the following objectives were studied:

I) Online combustion of liquid organic solvents in a commercial carbon analyzer oven in an oxygen-rich atmosphere to convert the samples into carbon dioxide. This is a crucial step prior to introduction of samples to ICP in order to prevent high solvent loads in the plasma, soot formation on the wall of the torch, and plasma extinction.

II) Evaluation of three different gas separator devices (NaOH falling-film column, hollow fiber gas exchange device, and PTFE membrane based aerosol desolvator) to remove the CO_2 and the remaining oxygen prior to introduction of the gas stream into the ICP.

III) Evaluation of this novel approach for the analysis of volatile organic substances by ICP-OES.

IV) Investigation of the effect of small amounts of CO_2, which may pass the removal section, on the signal intensity of various elements and plasma robustness.

1.2 General Introduction

The inductively coupled plasma (ICP) is considered as an atomization, ionization, and excitation source which is used in combination with either optical emission spectrometric (OES) or mass spectrometric (MS). Inductively coupled plasma optical emission spectrometry is a powerful tool for the determination of trace, minor, and sometimes major elements in a wide range of sample matrices [1-10]. It has been demonstrated that the composition of the sample matrix could cause alteration in the emission intensity of the analyte. In particular, this alteration may affect the accuracy and precision in the quantification of trace elements [11-13]. The matrix interferences can be produced by inorganic acids [11], easily ionizable elements [12], or organic solvents [13-17]. In ICP-OES, spectral interferences due to the presence of low amount of organic solvents in the plasma are, usually, not a limiting consideration for trace elements analysis, since the number of analytical lines that could suffer from potential spectral interferences are quite low [18, 19]. The importance of direct analysis of organic samples using ICP in order to determine trace elements has been well documented [20]. There are main circumstances in which the introduction of organic samples into the ICP are required or desired:

I) For the direct analysis of trace elements in petroleum feedstocks and petroleum products [21-31]
II) For the determination of wear metals in used aircraft lubricating oils, to indicate engine deterioration [30, 31]
III) For analysis of organic extracts [32-39]
IV) For the quantitation of trace elements in waters after extraction into an organic solvent [40]
V) After a sample pre-treatment (sample dissolution, solvent extraction, etc.) [22]
VI) After a previous chromatographic step in the analysis of environmental, biological, metabolic and pharmaceutical samples [41-50]

In recognition of the importance of non-aqueous ICP-OES, studies have been reported that the behavior of the ICP with organic solvents is different from that with aqueous solutions [13-15]. It is recognized, however, that owing to the greater volatility of many organic solvents compared to water, for ICPs fed with organic the experimental conditions for stable plasma operation are much more critical than with aqueous solution [18, 35, 40-43, 51-53]. A number of more fundamental studies have identified a range of potential problems associated with the introduction of organic solvents into the plasma [18, 54, 55]. These problems have been described in the following section.

1.3 The problems of ICP-OES with organic solvents

1.3.1 Plasma ignition

Introduction of volatile organic solvents into the plasma produce high solvent loads which can cause soot formation on the wall of the torch or even plasma extinction [1]. Therefore, the generation of plasmas that are stable over prolonged periods of time is the first problem to be solved in analysis of organic solvent solutions [54]. Miyazaki et al. applied a specific ignition procedure for 32 organic solvents and reported that for about one third of the considered solvents plasma ignition was very difficult or even impossible [56].

1.3.2 Spectral interferences

Previous studies illustrated an enhancement in background emission with introduction of organic solvent in the ICP compared to aqueous solutions [26, 57-63]. Spectral interferences, due to C_2-and CN-band emission, have been reported for the determination of trace elements in organic solvents [14, 18, 64, 65]. However, for low concentration of organic solvents, the numbers of analytical lines that suffer from potential spectral interferences are relatively low and spectral interferences are usually not a limiting consideration for trace elements analysis by ICP-OES [13, 18, 19, 26].

1.3.3 Changes in the aerosol generation process

Organic solvents mainly affect the pneumatic nebulization process due to their significantly lower surface tension, higher viscosity and vapor pressure when compared to water [67]. As a result, aerosols become finer than those obtained with plain water solutions [68]. Similar results have been reported using different types of nebulizers [69].

1.3.4 Changes in discharge characteristics

Introduction of organic solvents into the ICP change the characteristics of the discharge significantly when compared to an ICP with aqueous aerosol. Due to the formation of the C_2 a green ‘’tongue’’ in the aerosol channel is observable. Dissociation of the green tongue at about 8-12 mm above the load coil and formation of CN and CO cause the disappearance of the green tongue. Air surrounding of the discharge would be the N_2 and O_2 source [70]. The important variable operational parameters which need to be optimized are:

I) Radio frequency (RF) input power
II) Argon gas flow rates
III) Observation height
IV) Sample feed rate
V) Torch geometry

VI) Addition of oxygen to the inner, intermediate or outer gas flow of the ICP torch

1.3.5 Changes in excitation temperature and analyte signal

The excitation temperature, T_{exc}, is the temperature that governs the energy population as defined by the Boltzmann distribution [7]. Kreuning and Maessen [71] used Fe (II) emission lines for measuring the excitation temperatures for different organic solvents. These authors found that excitation characteristics strongly depend on the solvent load and the nature of the pyrolysis products. By introducing chloroform and carbontetrachloride, Boorn and Browner [18] observed a change in excitation conditions when compared with water. These authors assumed large vapor loading, produced by these highly volatile solvents, absorb the RF power in the central channel and consequent temperature decrease in the plasma. Benli [72] illustrated that for ethanol/water mixtures, by increasing the ethanol concentration in ethanol-water mixtures from 0 to 90 % v/v, firstly the excitation temperature slightly increased and then reached the highest level and finally dropped to a value lower than that obtained with pure aqueous solutions. Goldfarb et al. [73] also observed a decrease in the plasma temperature by introducing the ethanol into the plasma. Blades et al. [70] measured excitation temperatures for an ICP with both water and xylene introduction. These authors observed a lower excitation temperature for a xylene aerosol than an aqueous aerosol at a fixed power and observation height.

Previous study showed 50-200 % net analyte signal suppression in the presence of certain volatile organic solvents [18]. This signal suppression is due to the changes in plasma excitation characteristics caused by interaction of solvent with the plasma and subsequent lowering its excitation temperature.

In order to alleviate these problems the following changes compared to the introduction of aqueous samples have been reported in literatures which have been listed in the following section.

1.4 Measures taken to alleviate interferences with organic solvents

1.4.1 Control of solvent load

For elimination of carbon build-up and abnormally high nebulization efficiencies, the solvent load of plasmas can be reduced by reduction of the sample uptake rate [18, 74] or by reduction of the aerosol carrier gas flow rate [54, 75] or by cooling of the aerosol [15, 18, 21, 41, 54-57, 62, 71, 76-78]. The aerosol can be cooled by the use of a condenser [15, 18, 54, 56, 57, 62, 71, 76-78] or by spray chamber cooling [59]. Both methods remove significant proportions of the solvent from the aerosol by condensation. It has been proved that temperature fluctuation in the spray chamber can have a significant effect on the signal intensity, especially for organic solvents with high vapor pressure [56, 79]. The accuracy of the analytical signal will be improved using a spray chamber whose temperature is retained constant [79].

Some authors have recommended that for common solvents such as methyl isobutyl ketone (MIBK), petroleum ether, xylene, ethanol and benzene the spray chamber could be run easily at 8-10 °C. For more volatile solvents such as acetone or chloroform lower temperature would be required and the chamber can be operated below 0 °C [79]. Haueler and Taylor developed a cooled spray chamber for measurements of 15 different elements in toluene [41] and in pyridine [42]. The detection limits at 0 °C was 0-100 times lower for toluene compared to room temperature. In previous studies, it has been demonstrated that aerosol cooling improves the signal-to-background ratio of more than two orders of magnitude for various combinations of spectral lines and organic solvents [41, 56]. However, such gains refer to improvements with respect to the generally very poor signal-to-background ratios obtained with certain organic solvent solutions.

1.4.2 Increasing the RF power

It has been found that the major difference between optimized ‘’aqueous ICP-OES’’ and optimized ‘’organic ICP-OES’’ is in the magnitude of the RF input power [13]. Organic solution plasma usually operates at higher power than aqueous solution plasma. In order to stabilize the discharge and to achieve similar excitation conditions, 500 W of additional power is required with organic solvent introduction compared to aqueous sample introduction. The reason for this difference is higher energy consumption for the decomposition of organic compounds than the decomposition of water [18]. Boumans et al. [13] investigated the effect of xylene on ICP characteristics. They showed that the presence of organic solvent increases the enthalpy of the carrier gas, and, after molecular dissociation, species like C_2, CN and CO enhance the thermal conductivity of the aerosol channel. This suggestion is supported by results published by Blades and Caughlin [70] who measured the excitation temperatures for an ICP with both water and xylene solvent introduction. These authors demonstrated a lower excitation temperature for the organic solvent ICP than for the aqueous solvent ICP at a fixed power and observation height. They illustrated a decrease in the excitation temperature, due to the absorption of RF power by the large vapor loading of organic solvent and subsequently the dissociation of C-molecules in the central plasma channel.

Barrett and Pruszkowska [26] illustrate the effect of RF power on the intensity of atom and ion lines using xylene as a solvent. These lines were selected in a wide range of excitation potentials from 2.9 eV to 15.4 eV. These authors reported that for the lines with excitation potential higher than 13 eV intensities of lines slowly increase with increasing the power, while intensities of lines with lower potentials show slight variation with power. Moreover, they demonstrated that by enhancing the RF power in organic ICP, the intensity of the C line increases, the intensity of the C_2 band decreases, and the CN emission signal is generally stable. The power enhancement increases the amount of energy available in the plasma and promotes dissociation of organic solvent, thus reducing C_2 emission and subsequently increasing C emission. Generally, effect of increasing the incident power is to help the dissociation of organic matrix.

1.4.3 Increasing the outer gas flow

In order to prevent torch melting due to the increased RF power, increasing in the outer gas flow is necessary. Moreover, it is desirable to use a high outer gas flow to prevent carbon deposition and maintain more stable plasma [75].

1.4.4 Addition of a low flow of oxygen into the nebulizer and outer gas flow

Due to the high solvent vapor load, organic solvents can form carbon deposits in ICPs. In ICP-OES, in order to eliminate soot formation, prevent C deposition and reduce CN and C_2

molecular band emission, sometimes addition of oxygen into the carrier argon stream causes solvent vapor combustion. In ICP-MS for removing the green C_2 emissions observed at the base of the plasma and preventing soot formation on the cooled sampling cone, a small dose of O_2 is often added to the nebulizer, intermediate or outer gas flows [79]. The addition of oxygen increases polyatomic interference problems from metal oxide ions (MO^+) and it may cause the sampling cone degradation. Therefore oxygen addition in ICP-MS must be carefully controlled [1, 21, 22, 57, 58, 63, 79-101].

1.4.5 Decreasing the injector diameter

It has been reported that by using a smaller injector inner tube diameter with organic solvents analysis, the plasma stability improved and the base line noise reduced. In this case, the pressure in the spray chamber and the velocity of sample aerosol introduced into the plasma is higher which causes the reduction of interaction time with the ICP. Barrett and Pruszkowska [26] reported that the selection of appropriate injector tube size depends on the type of solvent. These authors showed that common solvents such as kerosene, xylene, and chloroform using an injector tube of 1.5 mm or less generate a symmetrical plasma and a stable discharge and for more volatile solvents such as methanol and MIBK the size of 1.0 mm or less.

1.4.6 Increasing the nebulizer gas flow

Boumans and Lux- Steiner [13] reported that for ICP loaded with organic solvents an intermediate gas flow is required in order to prevent soot formation on the inner surface of the torch. By operating the plasma at higher nebulizer gas flow, the aerosol drop size distribution becomes finer and the aerosol transport efficiency to the plasma improves.

1.4.7 Using of desolvation systems to remove large percentage of organic solvents

Removal of the solvent after nebulization by using the aerosol cooling/desolvation approach is a general solution to minimize the problems of organic solvents introduction [1, 102, 103]. The basic principle of the desolvation system is that, after nebulization, the aerosol will be heated to maintain the sample in a vapor phase. Afterwards, the sample vapor enters to a cooler/condenser or a membrane desolvation system in order to reduce the amount of solvent entering the plasma.

By cooling the sample vapor, the amount of solvent entering the plasma can be reduced and is particularly useful when it comes to analyzing some volatile samples. This cooling can be a few degrees below ambient or as low -20 ºC, depending on the types of sample being analysed. The trapping of analyte in the condenser will increase with decreasing condenser temperature resulting in degraded analytical performance (limit of detection (LOD), and limit of quantitation (LOQ)) [54].

Membrane desolvation devices are very useful for aqueous-type samples, but more important for volatile organic solvents. The design of a fully optimized desolvation system depends on the application. Various factors such as the solvent and its physical parameters, the solvent volume flow rate, the degree of solvent removal and the solvent tolerance of the ICP will determine the performance of the desolvation system [104].

1.4.7.1 Various desolvation systems

In order to reduce solvent load into the plasma several separators and desolvation systems such as separator modules, cryogenic desolvation, desolvation interfaces and membrane interfaces have been reported in previous studies. Below is the brief description of these various desolvation systems:

1.4.7.1.1 Separator modules

Separator modules are Peltier-based aerosol cooling devices to be installed between the spray chamber and the ICP torch. This device is built from three separate electronic cooling modules. This electronic aerosol cooling device has recognized to be more appropriate than an aerosol cooling device containing a coiled aerosol cooling tube dipped in a liquid cooling bath. Additional advantages of this device include simplicity in the design, stability, easy operation and flexibility to automation [76]. Although these separator modules provides temperatures stable to ± 0.5 ºC for as long as is needed, limited temperature range is the main disadvantageous of this device.

1.4.7.1.2 Cryogenic desolvation

Cryogenic desolvation is usually a two-step system. In the first step, the aerosol is transporting through a primary condenser kept at either 0 or -10 ºC. In the second step, after exiting the primary condenser, the aerosol stream is passing through a low-temperature cryocondenser, which is cooled by dry ice (~-80 ºC) [105]. By using this cryogenic desolvation, solvent load decreases to such an extent that a single set of conditions could be applied for a range of solvents. Higher RF powers, sample delivery restrictions, special torches and plasma ignition conditions are not required for sustaining of stable plasma.

1.4.7.1.3 Membrane interface

Gustavsson [106] developed a membrane sample introduction interface, designed especially for removing organic solvents from aerosols. In this study a silicone rubber membranes with an active area of 40×400 mm was used. With this membrane an acceptable solvent removal was achieved at a separator temperature of 20 °C. The organic solvent removal in this device is quite efficient and also gives adequate analyte transport efficiency. In another study, Bäckström and Gustavsson [107] used two membranes with thicknesses of 12 and 15 µm. Their investigation showed that by using a thicker membrane the solvent removal efficiency was decreased. Moreover, they showed that organic solvents with different polarity and volatility can be handled by this membrane. The main advantageous of this membrane is that all the gas flow rates and the liquid flow rate can be changed independently therefore its performance is easy to optimize.

1.4.7.2 Benefits of desolvation system

Removing organic solvents from the aerosol leads the following benefits:

I) Similar excitation properties (i.e., background spectra and analyte line intensities) for both organic solutions and aqueous solutions at the same forward power [78]

II) Reduction of matrix-derived background emission and enhancement of the analyte signal and detection limit [108]

III) Operation of the ICP with organic solvent samples of different polarity and volatility [107]

IV) Application of nebulizers with higher analyte transport efficiency [107]

1.4.7.3 Problems and peculiarities of desolvation system

For analysis of various organic solvents, several problems and difficulties were noted in experimentation with the desolvation systems. Chemical species which are partially or completely volatile at temperatures close the temperature of the desolvator heater will be condensed and removed to a variable level in the membrane desolvator resulting in imprecise or totally misleading results. Prior to analysis, by chemical means, volatile analyte forms must be rendered non-volatile. It has been reported that non-volatile analytes in sample solutions may cause gradual fouling of the desolvator as it deposits in the membrane pore structure [76, 105-108].

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Part 2

ONLINE COMBUSTION FOLLOWED BY CO_2 REMOVAL: EVALUATION OF A NEW APPROACH FOR THE ANALYSIS OF VOLATILE ORGANIC SUBSTANCES BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

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Authors: H. Wiltsche*, F. Moradi, P. Tirk, G. Knapp

(Selected for the cover photo of the journal)

2.1 Abstract

A novel online combustion system was developed for the quantification of metals (Ag, Cd, Cr, Fe, La, Li, Mg, Ni, Pb, Y, Zn, and Zr) in volatile organic solvents such as acetone, MIBK, chloroform, dichloromethane, tetrachloroethane or trichloro-trifluoroethane. After combusting the sample aerosol in a commercial carbon analyzer oven in an oxygen-rich atmosphere, carbon dioxide and remaining oxygen was removed from the gas stream prior the introduction into an ICP-OES. The proposed combustion/carbon removal approach allowed stable operation of the ICP even when introducing highly volatile solvents that otherwise would have immediately extinguished the plasma. Analyte signals in halogenated solvents were found to be significantly higher than in non-halogenated ones and non-linear calibration functions were observed for all investigated analytes below 5 mg kg^{-1}. Though a stable operation of the plasma was possible, the analyte signal intensities obtained in water were, depending on the element and the solvent, between 1.5 and 2800 times higher than in halogenated solvents.

2.2 Introduction

As described in Part 1, the introduction of volatile organic substances (e.g. solvents) into the inductively coupled plasma can be troublesome. Reduced plasma stability, structured plasma background from molecular species (e.g. C_2 or CN bands), spectral interferences by carbon and soot formation on the torch or the injector are some of the problems regularly encountered in ICP-OES when introducing larger quantities of carbon. The decomposition of the organic solvents by the ICP requires more energy compared to water [1] giving rise to a shift of the longitudinal emission maximum but there are disadvantageous with increasing RF power [2, 3]. On the one hand, high RF power increases the ICP's plasma continuum but on the other hand RF generators of contemporary ICP-OES and ICP-MS instruments can rarely provide more than 1700 W. This is rather low when compared to high powered, nitrogen cooled plasmas. These sources are reported to tolerate high solvent plasma loads without compromising the stability of the discharge. Greenfield et al. [4] used 5.5 kW RF power and a heated spray chamber to analyze samples of organophosphorus compounds dissolved in xylene. He also demonstrated that by changing the outer gas flow (coolant gas) to oxygen and increasing the RF power to 6 kW, C_2 and CN molecular bands could be effectively suppressed [5].

In this work a novel approach has been investigated to overcome the various problems of organic solvents, described in Part 1. The solution for solving these problems is to burn solvent and sample in the presence of oxygen and remove both, the evolved carbon dioxide and the remaining oxygen before the introduction of the gas stream into the ICP. The aim of this investigation was to evaluate the feasibility of this approach.

2.3 Experimental

2.3.1 Multi EA® 5000

The Multi EA® 5000 (Analytik Jena, Germany) is the new generation of elemental analyzers. The instrument is intended for the determination of total carbon, nitrogen, sulfur and chlorine. Liquid, solid and gaseous samples can be analyzed directly and without pretreatment. In this study we present a new application of this instrument.

This instrument is equipped with a double furnace technology which can be switched between vertical and horizontal applications, i.e. fast and optimum adaptation to the sample matrix and analysis standard with the least effort. In this work, the furnace in vertical position was used for combusting the organic solvents prior to introduction into the ICP. The Complete combustion occurs by means of intelligent procedure control in which the organic solvent is first pyrolyzed using inert gas. The pyrolysis products are then burned in the pure stream of oxygen to prevent the soot formation and make a guarantee for the actual oxidation process (This section is an additional description that has not been published).

2.3.2 Online combustion system

The online combustion system has been shown in Figure 2.1 comprised Multi EA® 5000 and a separation device for carbon dioxide removal. This setup was installed between the aerosol exit of the spray chamber and the torch of the ICP. The sample aerosol was mixed with additional argon and oxygen in the carbon analyzer oven where the combustion took place at 1050 °C, effectively burning all carbon to CO_2. The oven temperature was not optimized as it only needs to be high enough to ensure complete combustion. The instrument manufacturer's recommendation of 1050 °C was used throughout. The flow of argon and oxygen added to the aerosol during combustion was optimized in a way that deposition of soot in the oven was avoided even when introducing MIBK or dichloromethane. Detailed operating conditions of the oven are listed in Table 2.1. The main component of the combustion oven is the combustion tube consisting of two concentric quartz glass tubes. The sample aerosol is introduced into the inner tube, mixed with Ar and – depending on the experimental conditions – O_2 and heated. In this tube the sample undergoes a pyrolysis process in a “fuel-rich” atmosphere. The pyrolysis products leave the inner combustion tube through slots at the bottom and enter a very oxygen-rich atmosphere enclosed by the outer combustion tube. Here the combustion is completed.

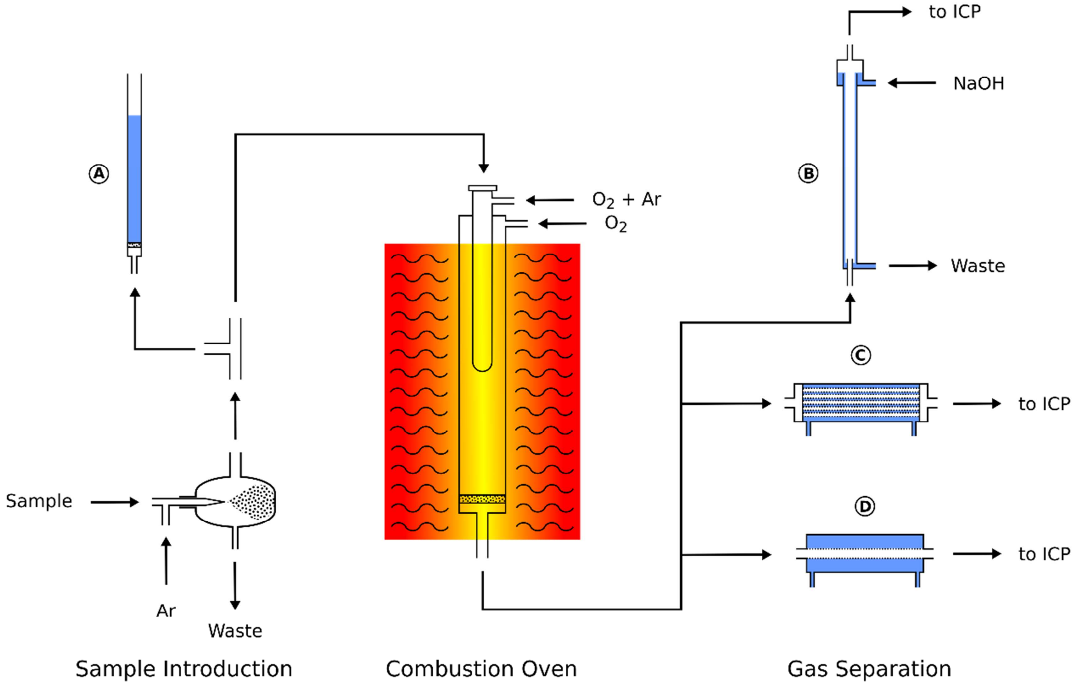

Figure 2.1: Schematic of the online combustion system. A) overpressure safety system, B) falling film column, C) hollow fiber gas exchanger, D) PTFE membrane desolvator.

The polytetrafluoroethylene (PTFE) membrane filter commonly installed at the exit port of the combustion oven had to be removed. Due to the glass frit inside the combustion tube the oven operates at a slight overpressure of about 0.05 bar. For security reasons a T-piece was installed in the aerosol transfer tube connecting the spray chamber to the oven entrance. The third port of the T-piece was connected with a small inner diameter PTFE tube to a water filled glass tube (Figure 2.1 A). By adjusting the water level inside this tube any inadverted pressure increase inside the combustion oven (e.g. soot deposition on the glass frit) could be detected by the appearance of gas bubbles.

In this work three means of removing the carbon dioxide from the aerosol that left the oven were investigated:

First, a falling-film column was built from a 0.8 m glass tube with an inner diameter of 20 mm. The aerosol entered the vertical column through a glass tube (5 mm i.d.) from the bottom while a thin film of 10 g L^{-1} NaOH solution was flowing down the column wall (Figure 2.1 B) and absorbing the CO_2 from the gas stream.

In addition, two membrane based gas exchange devices were examined: a hollow fiber gas exchanger (HMM0004 P84HS, Evonik, Austria) containing a 60 cm long fiber bundle of about 48 mm diameter (Figure 2.1 C). The fibers were installed inside a stainless steel tube that could be flushed with an argon sweep gas stream. The aerosol passed through the hollow fibers and CO_2 and O_2 was removed by diffusion. The second gas exchange device (Figure 2.1 D) was a commercial PTFE membrane desolvator (MDX200, Cetac Technologies, USA). The sweep gas exit port of both membrane based gas exchange devices was vented into a fume cupboard as – depending on the solvent used–Cl_2, HCl or in some cases HF was released.

After combustion and subsequent treating of the aerosol in either the falling film column or in one of the gas exchange devices, it was transported to the ICP torch by a 1.5 m PTFE tube (5 mm i.d.).

Table 2.1: Optimized combustion conditions

Instrument and parameter	Value
Oven	
Multi-purpose combustion tube	
Combustion tube temperature	1050 °C
Combustion tube outer gas flow	0.3 L min^{-1} O_2
Combustion tube inner gas flow at the "post combustion phase"	0.07 L min^{-1} O_2 + 0.13 L min^{-1} Ar
Membrane desolvator	
Sweep gas flow	1.0 L min^{-1} Ar
Membrane temperature	130 °C

2.3.3 Instrumentation

All measurements were carried out using an axially viewed ICP-OES (CIROS Vision EOP, Spectro, Germany). The operating conditions are reported in Table 2.2 unless otherwise stated.

Table 2.2: ICP-OES operating conditions

Spectrometer	Paschen-Runge mount with 22 CCD line detectors
RF generator	Huth-Kühn power oscillator
Torch	Standard torch, injector with 2.5 mm i.d.
RF Power	1650 W
Outer gas flow	14.5 L min^{-1}
Intermediate gas flow	0.6 L min^{-1}
Nebulizer gas flow	0.3 L min^{-1}
Spray chamber	Cyclonic; baffled and cooled to -20.0 ± 0.5 °C
Nebulizer	Mira Mist, Burgener Research, USA
Peristaltic pump tubing	Glass Expansion Tygon MH 2075; 0.64 mm i.d.

The samples were nebulized in a cooled spray chamber to avoid excessive solvent load in experiments without combustion. The selected ICP operation conditions maintained a stable discharge even under conditions of high carbon loading. For the sake of comparability between different experiments the cooled spray chamber and the same ICP operating conditions were used throughout this work.

2.3.4 Additional diagnostic techniques

The oxygen concentration in the gas stream leaving the membrane desolvator was quantified using a fiber-optical oxygen meter (Firesting O_2, Pyro Science, Germany) equipped with a retractable optical mini-sensor (OXR430, 430 µm fiber diameter, Pyro Science, Germany). Sensors calibration was checked with pure nitrogen and a premixed calibration gas (20 % O_2, 80 % N_2, Linde, Austria).

The carbon dioxide concentration in the gas stream leaving the membrane desolvator was determined using a dual-channel non dispersive infrared CO_2 sensor module (General Electric Telaire T6615, USA). Pure nitrogen (5.0 quality, Linde, Austria) and a premixed calibration gas (2 % v/v CO_2 in N_2, Linde, Austria) were used for CO_2 sensor module calibration.

The nebulization efficiency and mass flow of the solvent introduced into the ICP were determined using the well-established method of continuous weighing [6] as shown in Figure 2.2 (This figure is an additional illustration that has not been published). Briefly, sample was pumped from a glass beaker to the nebulizer and spray chamber where the aerosol was formed. Some of the liquid then left the spray chamber via the aerosol exit port whereas the rest was pumped from the drain port of the spray chamber back to the beaker. The beaker itself was placed on a balance (Sartorius AC210S) and the amount of liquid per unit of time that left the spray chamber as aerosol could be determined by recording the weight of the beaker as a function of time. The balance was put in a continuous weighing mode and sent the weight every 200 ms to a computer. For volatile solvents the evaporation from the glass beaker caused a small but significant error. Therefore the nebulization efficiency data were corrected by the evaporation rate of solvent from the beaker.

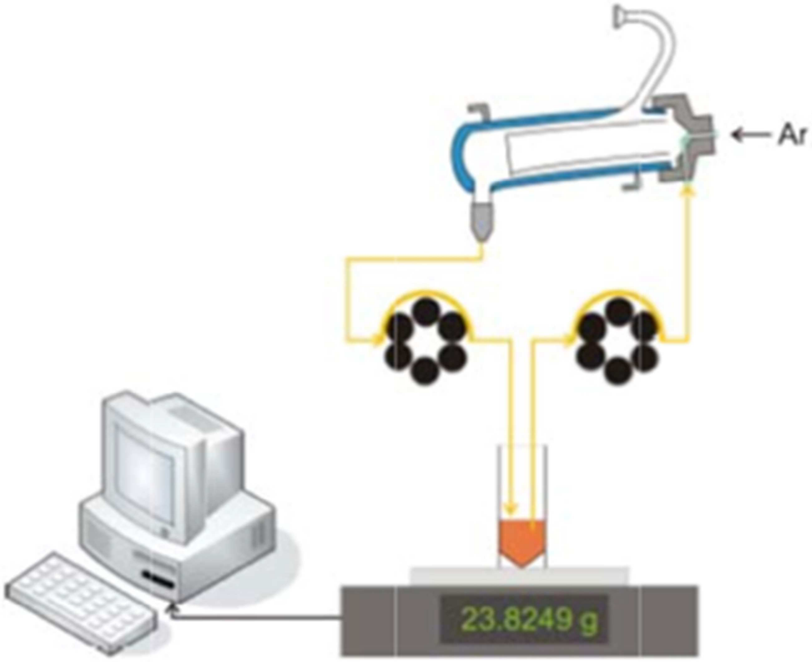

Figure 2.2: Schematic drawing of the direct weighing setup

2.3.5 Reagents

Solvents of p.a. quality were used throughout. Standards were gravimetrically prepared from oil- or toluene-based single element metallo-organic solutions (Cr, Fe, Mg, Ni: Conostan; USA; Cd, Pb, Y, Zn: Alfa Aesar, Germany; Ag La, Li: VHG Labs, USA) with a concentration of 1000 mg kg^{-1}. Aqueous multi element solutions were prepared from a commercial 100 mg L^{-1} 28 element stock solution (Al, Ag, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn in 5% HNO_3, Roth, Germany) and high purity water (18 MΩ cm^{-1}, Barstead Nanopur, Thermo Fisher Scientific, USA).

2.4 Results and discussion

2.4.1 Solvent loading of the ICP

It is well known [3, 6-9] that due to differences in viscosity, density and surface tension the nebulization efficiency of organic solvents is usually higher than that of water. Using the conditions reported in Table 2.2 the aerosol solvent load and the corresponding nebulization efficiency and aerosol carbon load were determined by the method of continuous weighing [6] for a number of common organic solvents. The results listed in Table 2.3 clearly show that the nebulization of solvents like acetone or diethyl ether will cause heavy carbon loading of the ICP whereas methanol or butanol represent a lower burden for the plasma.

Table 2.3: Nebulization efficiency, aerosol solvent load and aerosol carbon load of selected solvents

Solvent	Nebulization efficiency, %	Aerosol solvent load, mg solvent min^{-1}	Aerosol carbon load, mg C min^{-1}
Acetone	11	96	60
Dichloromethane	17	258	37
Diethyl ether	47	297	193
Butanol	3.7	32	21
Methanol	5.9	50	19
MIBK	6.2	51	37
Water	2.4	46	-

2.4.2 Effect of oxygen on the ICP

The introduction of molecular gases like oxygen is known to affect the excitation properties of the ICP [11, 12]. Compared to other approaches, where a small flow of oxygen [13, 14] (a few ml min^{-1}) was added to the intermediate or inner gas flow of the torch to avoid soot deposition, the setup used in this work operated at a much higher oxygen concentration to facilitate complete combustion and avoid soot-induced clogging of the oven.

As the combustion oven always adds argon and oxygen to the aerosol prior and during combustion, the setup for studying the effect of oxygen on the ICP was slightly modified: the spray chamber was disconnected from the oven and the oven entrance was tightly sealed. The Ar/O_2 mixture (0.3 L min^{-1} O_2 and 0.2 L min^{-1} Ar; note that the combustion conditions in the final setup introduced even slightly more oxygen as listed in Table 2.1) leaving the exit port of the oven was then combined with the aqueous aerosol (10 mg L^{-1} multi-element solution) from the spray chamber and introduced into the ICP. To simulate the conditions without the presence of oxygen, the aerosol was mixed with 0.5 L min^{-1} Ar from an additional mass flow controller after the spray chamber, making up for the Ar/O_2 mixture that was otherwise added by the combustion oven. Keeping the gas flow in the ICP-torch’s injector constant was considered to be important, as it is well known, that the gas velocity inside the plasma's analytical channel is of significance to the emission signal.

The effect of oxygen on the ICP is rather deleterious as shown in Figure 2.3. Although the RF power in all experiments was very high (1650 W) the introduction of oxygen by the combustion oven resulted in a suppression of atomic emission lines by a factor of 2 to 9 whereas ionic line emission was reduced 9 to 60 times when compared to the emission signal of the same line in the absence of oxygen. It is interesting to note, that with exception of the two Ar (I) emission lines investigated (404.442 and 430.010 nm; line energy 14.7 and 14.5 eV, respectively) all atom emission line suppression factors increase with the line energy. The reason for this behavior could be a significant change in the ICP's excitation temperature. Clearly, the presence of larger volume fractions of oxygen in the carrier gas stream entering the ICP should be avoided.

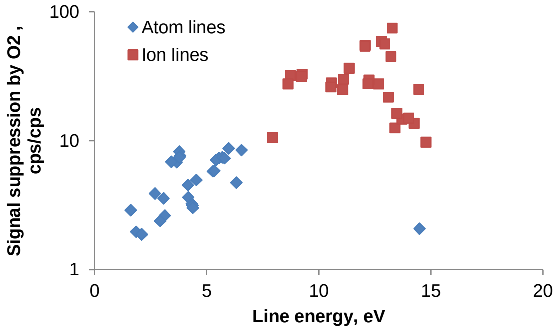

Figure 2.3: Signal suppression of 56 emission lines (presented in Appendix B) by 0.3 L min^{-1} oxygen as a function of the emission line energy. An aqueous 10 mg L^{-1} multi-element solution containing 28 elements was used. For atomic lines the excitation energy was used whereas for ionic lines the energy sum of excitation and ionization energy was plotted. Line energies are taken from [15]; Error bars are not plotted for clarity; RSD for all lines < 5 %; n=5; note the logarithmic scale.

2.4.3 Removal of CO_2 and oxygen after combustion

The experimental setup used for comparing the three gas treatment devices was similar: applying the conditions reported in Table 2.2, a solution containing 50 mg L^{-1} Ca, Cu, Co, Fe, Mg, Mn, Na, Ni, Ti, and Zn in butanol was nebulized in the spray chamber, the aerosol was then burned in the combustion oven and the gas stream that left the oven was passed through one of the gas treatment devices. Blank readings were obtained from pure butanol.

2.4.3.1 Falling-film column

The falling-film column was considered a cheap and easy way of removing carbon dioxide from the aerosol. Previous experience showed that with increasing NaOH concentration the removal efficiency of the column was improved, reaching a plateau at 10 g L^{-1} NaOH. Therefore, this concentration was used further on. Three setups using the falling-film column were investigated: in the first experiment the combusted aerosol was directed through the empty and dry column prior the introduction into the ICP. In the second experiment the walls of the falling-film column were constantly wetted by a stream of 10 ml min^{-1} NaOH solution and in the third experiment, the column was dried again and filled with 30 cm Raschig rings (5 mm diameter, 5 mm length). No liquid was employed in this experiment.

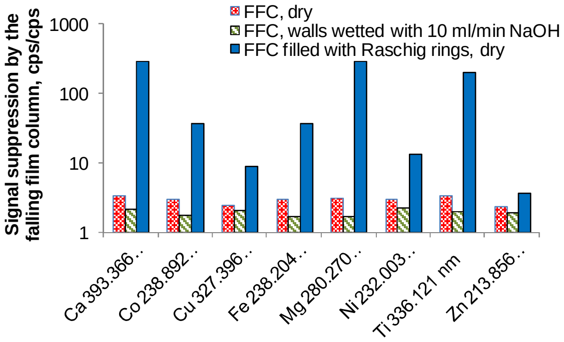

Figure 2.4: Signal suppression caused by the falling-film column at different conditions compared to the emission signal of each line when the aerosol leaving the combustion oven was directly introduced into the ICP. Error bars are not plotted for clarity; RSD for all lines < 5 %; n=5.

As shown in Figure 2.4 the falling-film column does not improve the emission signal of the investigated analytes. Much to the contrary, the signal loss – expressed as the ratio between the emission intensity without the column and the emission intensity with the column in place – is about a factor of 3 for the dry column and a factor of 2 for the wetted column. This behavior can be explained quite well when considering the huge signal losses in the presence of the Raschig rings inside the dry column: a large proportion of the water generated during the combustion is deposited on the Raschig rings. This causes a loss of a large fraction of the analyte aerosol, rendering the concept of a falling-film column in this application impractical. The slightly reduced signal suppression when using the NaOH solution can be attributed to a reduced carbon loading of the ICP as 18 % of CO_2 are removed from the gas stream. This is supported by the fact, that the plasma robustess [16] (Mg (II) $_{280.270,\ nm}$ /Mg (I) $_{285.213,\ nm}$ ratio) increased from 3.7 (without column) to 5.3 when the falling-film column was used.

Another severe disadvantage of the falling-film column is its inability to remove oxygen residues from the combustion oven. Though it might be possible to remove oxygen as well (e.g. by using a Fe^{2+} washing solution in a separate column) this concept would involve even more reagents and instrumentation.

2.4.3.2 Hollow fiber gas exchange device

The hollow fiber gas exchange device and the PTFE membrane-based desolvator are capable of removing both CO_2 and excess O_2 from the combusted aerosol by diffusion. Both devices rely on an argon sweep gas stream flowing countercurrent to the sample aerosol stream around the hollow fiber or PTFE membrane.

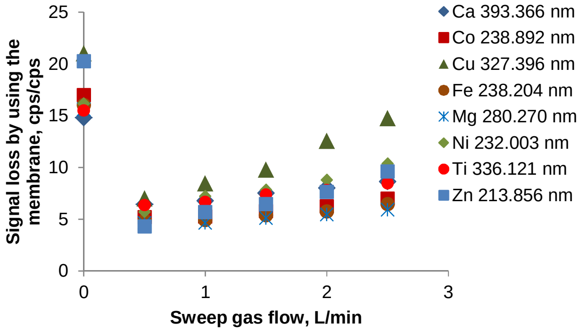

Figure 2.5: Signal loss using the hollow fiber gas exchange device as a function of sweep gas flow. The signal loss is defined as the ratio of intensities without/with the membrane. Error bars are smaller than the data points.

As shown in Figure 2.5, there is a loss in signal intensity by a factor of 13 to 21 when comparing the emission intensities without and with the hollow fiber membrane in place. Even at the optimum sweep gas flow of 0.5 L min^{-1} Ar, the emission signals are a factor of 3 to 8 lower than without the hollow fiber gas exchange device. Again, condensation of water in the gas exchange device's stainless steel body was observed, explaining at least partially the large signal loss in this device. Constrained by recommendations of the manufacturer, it was not attempted to heat the gas exchange device as this would have resulted in a system degeneration above about 70- 80 °C.

The reduced signal loss at 0.5 L min^{-1} Ar as sweep gas can be attributed to the removal of CO_2 (40 %) and O_2 from the aerosol. This is also reflected by an increase of the plasma stability (Mg (II)/Mg (I) ratio) from 3.6 to 6.1. Another increase in sweep gas flow to 1 L min^{-1} enhanced the plasma stability only slightly to 6.8 and remained unchanged until 2.5 L min^{-1}. Simultaneously, a steady element- dependent rise in the signal loss was observed that seems to be caused by the pressure gradient inside the membrane desolvator.

2.4.3.3 PTFE membrane-based aerosol desolvator

As condensation of water seemed to be the unifying problem of both the falling-film column and the hollow fiber gas separation device, a commercial PTFE membrane-based desolvation unit was investigated. In this unit the membrane can be heated to temperatures well above 100 °C. Thereby, water condensation is circumvented.

Initial experiments were conducted with a 2 m PVC transfer line (3 mm i.d.) connecting the membrane desolvator to the ICP. The PTFE membrane was heated to 110 °C and the argon sweep gas flow was varied between 1 and 2.5 L min^{-1} in steps of 0.5 L min^{-1}. As in all other experiments the emission signal of the investigated elements obtained without the membrane were used for signal normalization.

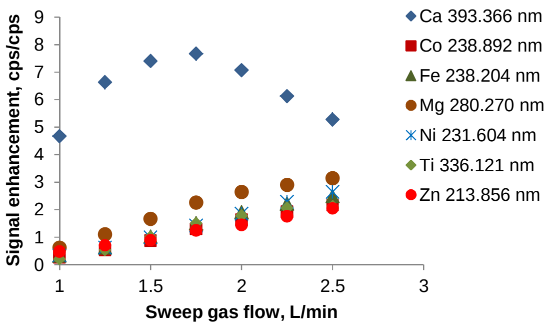

Figure 2.6: Signal enhancement by using the PTFE membrane desolvator. The signal enhancement is defined as the ratio of intensities with/without the membrane. Error bars are smaller than the data points.

The enhancement of the emission lines using the membrane desolvator is shown in Figure 2.6. Because of removing of CO_2 (99 %) and O_2 the emission intensity of all lines increased significantly. Due to the fundamental mechanisms of line excitation not all lines show the maximum enhancement at the same sweep gas flow.

The aerosol transfer line between the oven and the membrane desolvator was 0.2 m (5 mm i.d.) long and wrapped with aluminum foil, effectively preventing the condensation of water. In the final setup, the membrane temperature was increased to 130 °C.

From the above discussion it is evident that the PTFE membrane-based aerosol desolvator is the only viable way of removing carbon dioxide and oxygen. Both falling-film column and hollow fiber gas exchange device suffered from a significant analyte loss (about a factor of 10 to 100 for the falling-film column and a factor of 5 for the hollow fiber gas exchange device) due to condensation of water.

2.4.4 Optimization of the combustion conditions

The absence of oxygen in the inner combustion tube resulted in instable emission signal intensities as shown in Figure 2.7. Even 300 s after the introduction of a 1 mg kg^{-1} multi element solution in dichloromethane the signals of Fe, Li, Mg, Y, and Zn increased and stabilized only after about 400 s. Cr and Li showed a peculiar transient profile wherein the highest signal intensity was encountered immediately after the sample reached the oven for the first time following a decrease of both signals. The Li signal rose again slowly after a local minimum at about 105 s. This behavior might be explained with the formation of carbides: CrC is a refractory material with a boiling point of 3800 °C and lithium is also reported to form Li_2C_2 at temperatures above 1000 °C [17]. Initially, the inner surface of the combustion tube was not covered with carbon. Therefore Cr and Li were not retained in the inner combustion tube. As soon as soot started to build up in the inner tube, elements like Cr and to some extend Li were partially trapped reducing the respective emission signals. The fact that soot deposition inside the inner combustion tube was observed visually supports this theory. It is important to note, that after each measurement the combustion tube was cleaned by changing the inner gas flow of the combustion oven to 0.2 L min^{-1} oxygen for 45 s (so called “post combustion phase”). Thereby reproducible conditions where maintained between the individual sample runs.

Clearly, soot deposition must be avoided inside the inner combustion tube. Due to the completely different temporal analyte profiles the use of an internal standard cannot be expected to compensate for the effect of soot formation in multi-element analysis.

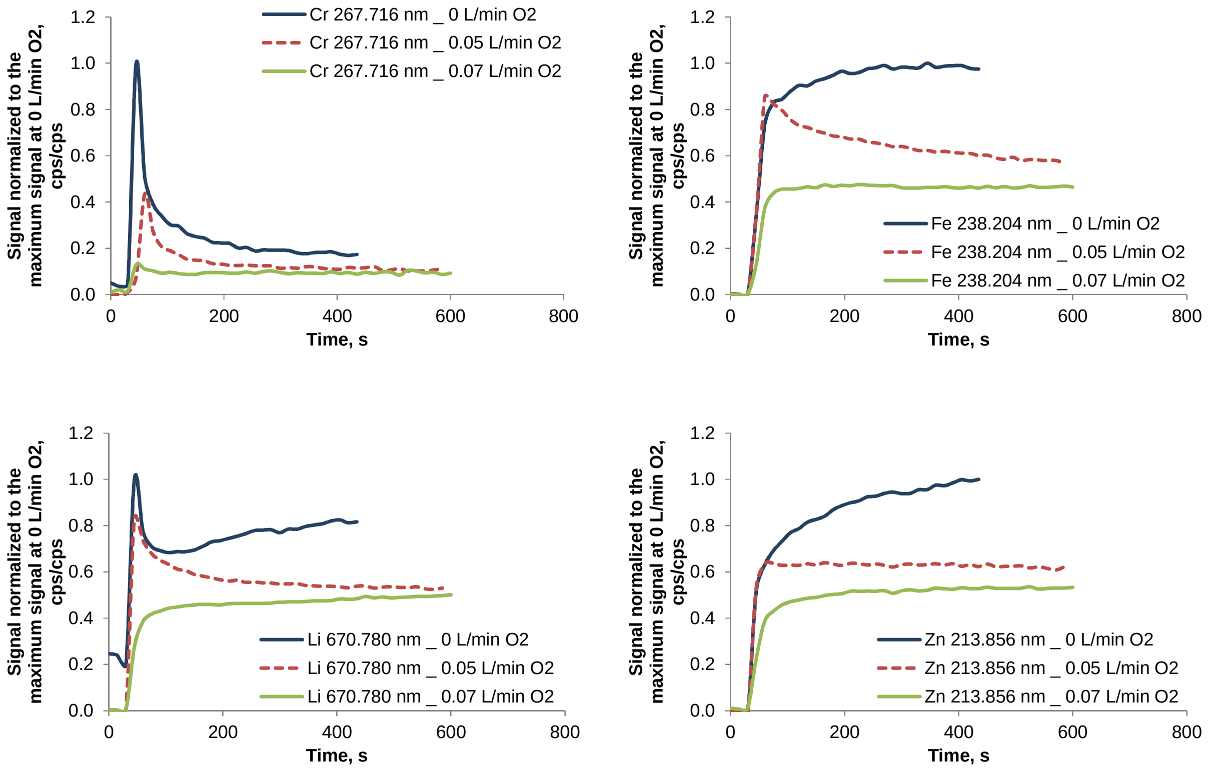

Figure 2.7: Signal response after the introduction of 1 mg kg^{-1} Cr, Fe, Li, and Zn dissolved in dichloromethane for different levels of oxygen in the inner combustion tube. The signals were normalized to the maximum obtained signal intensity at 0 L min^{-1} oxygen in the inner combustion tube. Note that it takes 45 s for the sample to be pumped from the autosampler cup to the spray chamber.

In order to avoid soot deposition in the inner combustion tube oxygen was also added during the analysis and not only during the post combustion phase. The fully computer-controlled oven allows the addition of oxygen to the inner combustion tube only in the post combustion phase. Consequently, the oven was programmed for a long post combustion phase of 700 s with either 0.05 L min^{-1} oxygen + 0.15 L min^{-1} argon or 0.07 L min^{-1} oxygen + 0.13 L min^{-1} argon in the inner combustion tube. For security reasons it was not attempted to increase the oxygen flow in the inner combustion tube above 0.07 L min^{-1}. It is interesting to note, that with 0.07 L min^{-1} oxygen + 0.13 L min^{-1} argon no soot formation was observed even with very volatile solvents.

With increasing amounts of oxygen in the inner combustion tube, the transient emission signals reached a steady state faster, as shown in Figure 2.7. For Ag, Ba, Cd, Cr, Fe, Li, Mg, Ni, Pb, Y, and Zn (not all data shown in Figure 2.7) a stable signal was reached after about 180 s when the gas mixture in the inner combustion tube was 0.07 L min^{-1} oxygen + 0.13 L min^{-1} argon. Further experiments were conducted using the same gas mixture.

With Y as internal standard the system's short term stability expressed as the RSD of 10 consecutive measurements of a 1 mg kg^{-1} Ag, Cd, Cr, Fe, Li, Mg, Ni, Y, and Zn standard in dichloromethane was between 1 and 6 %. Only for nickel the RSD was 8 %.

2.4.5 Composition of the gas stream introduced into the ICP

As noted earlier, oxygen and carbon dioxide have deteriorating effects on the ICP discharge. After the optimization of the combustion process and the membrane desolvator, the composition of the gas stream entering the ICP was investigated. It is important to mention, that any throttling of the gas stream had to be avoided as this would have resulted in a change of the membrane desolvator's pressure balance. Due to the alterations of the plasma's thermal conductivity [18] and the resulting changes in the ICP's excitation conditions any plasma-based spectroscopic quantification attempt for oxygen and carbon dioxide must be considered unreliable in the context of this work. Therefore, alternative spectroscopic techniques were used with dichloromethane as the representative test solvent.

When dichloromethane was introduced into the system under the optimized operating conditions reported in Table 2.1, the CO_2 concentration in the gas stream that left the membrane desolvator quickly rose to 0.16 % v/v and stabilized at 0.177 ± 0.002 % v/v (n=3) within 60 s. Upon stopping the introduction of dichloromethane to the spray chamber it took 180 s to reach baseline again as remaining solvent in the spray chamber continued to evaporate at low speed.

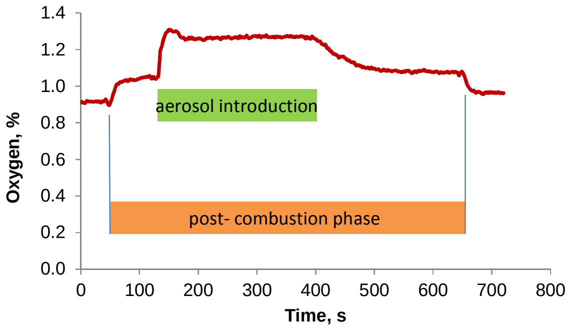

Figure 2.8: Oxygen concentration in the gas stream that leaves the membrane desolvator as a function of time.

The oxygen concentration in the gas stream that left the membrane desolvator was quantified using a fiber-optical oxygen meter (Firesting O_2, Pyro Science, Germany). It was found that the membrane desolvator removed the oxygen rather efficiently from the introduced gas stream. The aerosol entered the membrane desolvator with about 46 % oxygen and left it with no more than 1.3 %. The transient signal of the oxygen concentration in the gas stream that left the membrane desolvator showed a distinct profile: 30 s after the combustion oven program was started, the oven switched from the combustion phase to the post-combustion phase introducing 0.07 L min^{-1} oxygen into the center combustion tube. At this point the nebulization of the sample was initiated. The additional oxygen added in the post-combustion phase caused an increase in oxygen concentration of the gas flow that left the membrane desolvator. When the sample aerosol reached the combustion oven, the oxygen concentration in the gas stream that enters the ICP increased sharply (shown in Figure 2.8 after 130 s) to 1.28 % and then decayed swiftly towards a steady level of 1.26 % that remained steady until the introduction of sample to the spray chamber was stopped.

2.4.6 Influence of intramolecular chlorine on the metal release in the oven

The conditions during the combustion are characterized by the presence of a large excess of oxygen resulting in an increased formation of metal oxides. Upon passing through the glass frit located at the very bottom of the combustion tube, some of these oxides are potentially retained inside the oven. This theory is supported by the remobilization of metals by halogens: after the introduction of 50 mg L^{-1} Ca, Cu, Co, Fe, Mg, Mn, Na, Ni, Ti, and Zn in butanol, the signals of all analytes dropped to blank level within 45 s when switching to pure butanol and a blank measured immediately afterwards suggested no remaining contamination. A subsequent introduction of dichloromethane resulted in a detector saturation for all analytes. This indicates an instantaneous mobilization of metals trapped inside the combustion oven – most likely in the high surface glass frit installed at the lower end of the combustion tube. To further support the theory of metal releasing action of halogenes, solutions of constant analyte concentration but different ratios between a non-halogenated and a halogenated solvent (4-methylpentan-2-one - MIBK and dichloromethane respectively) were analyzed.

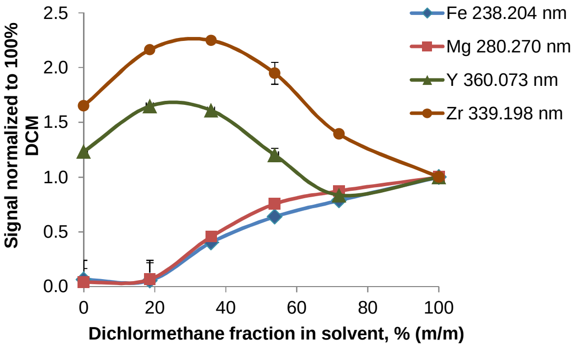

Figure 2.9: Variation of the analyte signal as a function of the solvent composition (MIBK/dichloromethane); n=3.

As shown in Figure 2.9 the analyte signals increased for Ag, Cd, Fe, Li, Mg, Ni, Pb, and Zn with rising concentration of dichloromethane. In pure MIBK the emission intensities of Ag, Cd, Fe, Li, Mg, Ni, Pb, and Zn were between 15 (Fe) and 4000 (Li) times lower than in pure dichloromethane. This clearly shows, that the presence of HCl and Cl_2, which are formed during the combustion, prevent the deposition of analytes in the oven. This is also apparent when considering that the melting points of all analyte chlorides are significantly lower than the corresponding oxides or carbides as listed in Table 2.4. For the chlorides of Cd, Fe, Pb, Zn, and Zr the boiling point is also lower than the combustion temperature leading to an efficient vaporization in the oven and high transport efficiency. In this context it should also be pointed out, that the RSDs for Ag, Cd, Fe, Li, Mg, Ni, Pb, and Zn decreased from 10–5 % to < 3 % when the dichloromethane content of the solvent mixture was increased from ≤ 18 % (m/m) to ≥ 38 % (m/m) dichloromethane. As even in pure MIBK the emission signals of these metals were at least 10 times higher than the SD of the background, the signal fluctuation causing the large RSDs must be attributed to other factors than the ICP.

Table 2.4: Melting and boiling point (at atmospheric pressure) of some substances potentially formed during combustion [17-19]

Substance	Melting point	Boiling point
Ag_2O	830 °C	
AgCl	455 °C	1557 °C
CdO	1559 °C; sublimation	
$CdCl_2$	568 °C	970 °C
CrO_3	Decomposes at 220 °C to Cr_2O_3	
Cr_2O_3	2266 °C	3000 °C
CrC	3000 °C	3800 °C
CrCl3	1150 °C	
Fe_2O_3	1565 °C	
Fe_3C	1650 °C	
$FeCl_3$	306 °C; sublimation starts at 120 °C	
Li_2O	1440 °C	
LiCl	610 °C	1360 °C
MgO	2800 °C	
$MgCl_2$	712 °C	1412 °C
NiO	1990 °C	
$NiCl_2$	968 °C; sublimation	
PbO	886 °C	1472 °C
$PbCl_2$	498 °C	951 °C
Y_2O_2	2440 °C	4300 °C
YCl_3	700 °C	1500 °C
ZnO	1975 °C	2350 °C
$ZnCl_2$	290 °C	732 °C
ZrO_2	2700 °C	4300 °C
ZrC	3250 °C	5650 °C
$ZrCl_4$	331 °C; sublimation	

Y and Zn signals obtained in pure MIBK were found to be 1.2 and 1.6 times higher than in dichloromethane. Nevertheless, moderate dichloromethane concentrations in the solvent increased the signals to 1.6-and 2.2-fold compared to pure dichloromethane. This is surprising as $ZrCl_4$ sublimates well below the oven temperature whereas YCl_3 boils at 1300 °C. Though the reason for this behavior is unclear, two mechanisms might be of importance: firstly, ZrO_2 and not $ZrCl_4$ can be the main Zr compound leaving the oven. As $ZrCl_4$ is commonly synthesized by treating ZrO_2 with carbon and chlorine at temperatures of about 900 °C [17], a lack of Cl_2 in the oven could prevent this formation. Secondly, $ZrCl_4$ might already hydrolyze partially to $ZrOCl_2$ inside the oven and thereby reduce its volatility. Summing up, the chemical reactions inside the oven are complex and depend on the solvent and the oven conditions used.

2.4.7 Calibration

Calibration functions of Ag, Cd, Cr, Fe, La, Li, Mg, Ni, Pb, and Zn in dichloromethane were recorded in the concentration range of 0 to 22 mg kg^{-1} (10 standards). All elements showed a non-linear behavior of the calibration functions for low concentrations as demonstrated in Figure 2.10. Though the precision of the 1, 3 and 5 mg kg^{-1} calibration standards was high (about 3 % RSD for all reported lines) a significantly lower slope was encountered than for the more concentrated calibration solutions. Above 5 mg kg^{-1} all analytes had a linear signal response except Cr and La. Similar behavior of the calibration functions was also observed in acetone, butanol, chloroform, MIBK, and tetrachloro- ethane. The calibration functions of Cr and La on the other hand were S-shaped. It is important to note, that this curvature of the calibration function at higher concentrations was found also for several emission lines of the same element (e.g. Cr (II) $_{205.552,\ nm}$ and Cr (II) $_{267.716,\ nm}$ or La (II) $_{333.749,\ nm}$ and La (II) $_{408.672,\ nm}$).

The element-independent onset of the linear section of the calibration function indicates an effect related to the sample introduction (combustion oven or membrane desolvator). As the analyte emission signals for standards of < 5 mg kg^{-1} were far higher than the plasma background (S/N >> 100), the curvature of the calibration function cannot be attributed to an approach towards the LOQ. To prove the possibility of analyte quantification even in this nonlinear region of the calibration function, a synthetic sample containing about 2 mg kg^{-1} of Ag, Cd, Cr, Fe, La, Li, Mg, Ni, Pb, and Zn in dichloromethane was investigated. 4 calibration standards in the range of 0.5 to 6 mg kg^{-1} were used to characterize a second order polynomial as calibration function. The determined concentration in the test sample was between 91 and 107 % of the target value for Ag, Cd, Cr, Li, Mg, Pb, and Zn. The signal of Fe was not significantly larger than the blank value (< 3 σ of the background). This experiment shows that even in the curved region of the calibration function analyte quantification is possible.

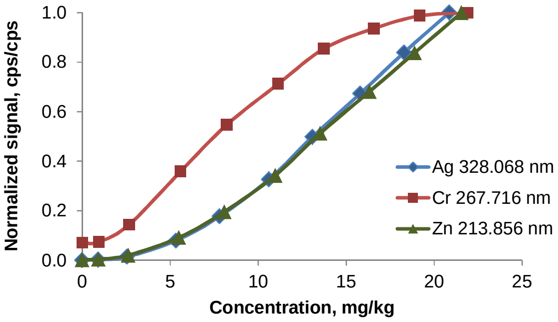

Figure 2.10: Calibration functions of Ag, Cr, and Zn in dichloromethane. Signals were normalized to the intensity of the highest calibration standard for comparability. Error bars are smaller than the data points.

It should be noted that due to the curvature of the calibration function at low concentrations any evaluation based on a linear regression model will fail. Also a second order polynomial – though applicable for the curved low concentration region – is not capable of modeling the linear dependence of the signal on the analyte concentration in the higher concentration range. Due to the lack of an applicable non-linear model, LODs and LOQs were not calculated. With exception of Cr and La all analytes showed a linear signal response up to the highest tested concentration of 70 mg kg^{-1} if the used emission line was within the linear detector range.

2.4.8 Analyte response for different solvents

Due to the non-linearity of the calibration function at low concentrations, the dependence of the analyte response on the used solvent is reported as sensitivity factors: by dividing the signal obtained from a solution of 10 mg kg^{-1} analyte in an aqueous standard by the signal of a 10 mg kg^{-1} analyte in an organic solvent, a sensitivity factor was calculated that allows the comparison between different solvents. The signal of the aqueous standard was obtained using the ICP conditions reported in Table 2.2 but without using the combustion oven and the membrane desolvator. In this experiment no oxygen was admixed to the sample aerosol resulting in a signal representing standard aqueous conditions. Thereby a comparison between aqueous and “organic solvent” conditions is possible.

In all investigated organic solvents the analyte emission intensities were significantly lower than those obtained for aqueous solutions as shown in Table 2.5. The direct introduction (cooled spray chamber only–no combustion or desolvation) of the volatile solvents such as acetone, chloroform, dichloromethane, tetrachloroethan and 1,1,2-trichloro-1,2,2-trifloroethane extinguished the ICP irrespectively of the plasma conditions used.

Table 2.5: Sensitivity factors for different solvents: this factor describes the magnitude of signal reduction, when analyzing the respective organic solvent using the combustion procedure compared to the “standard” aqueous sample introduction (spray chamber only). The sensitivity factor of water is 1 for all analytes. No internal standard was used; ND: not determined, SIF: spectral interference, NS: no signal detected (defined as $< 3\sigma$ of the blank emission signal).

Element Emission line, nm	Acetone	Butanol	Chloro-form	Dichloro-methane	MIBK	Tetra-chloro-ethane	1,1,2-trichloro-1,2,2-trifloro-ethane
Ag$_{328.068}$	ND	ND	6.4	8.2	4700	27	4.9
Cd$_{214.438}$	ND	ND	19	21	12000	84	15
Cr$_{205.552}$	ND	ND	590	320	110	2800	380
Fe$_{238.204}$	440	64	15	21	110	69	4.9
La$_{408.672}$	ND	ND	0.7	1.2	3.0	36	1.5
Li$_{670.780}$	7400	ND	6.7	9.6	ND	49	5.0
Mg$_{280.270}$	260	60	6.2	10	170	46	3.1
Ni$_{221.648}$	1000	99	17	19	460	69	SIF (Si)
Pb$_{220.353}$	ND	ND	57	70	2800	260	33
Y$_{371.030}$	ND	ND	1.0	6.0	3.0	16	4.2
Zn$_{213.856}$	3300	340	26	24	53000	110	2.4
Zr$_{343.823}$	ND	ND	2.8	3.5	2.2	14	0.3

The data shown in Table 2.5 support the theory of the transport efficiency enhancing property of halogens on several analytes: for Ag, Cd, Li, Mg, Ni, Pb, and Zn the sensitivity factors were between two and three orders of magnitude lower in halogenated solvents than in non-halogenated ones. This is also in good agreement with the findings presented in Figure 2.11. For Cr and Fe the transport efficiency enhancing effect of halogens was less pronounced and La, Y, and Zr were only affected to a small degree.

The lowest sensitivity factors were obtained in 1,1,2-trichloro-1,2,2-trifloro-ethane. In comparison to tetrachloroethane the presence of fluorine in the molecule suggests a more efficient release of metals from the oven. This finding is also consistent with the improved metal release observed in electro-thermal vaporization ovens in the presence of Freon [20]. It is worth noting, that the formed HF caused significantly increased Si background resulting in spectral interferences of the $Ni_{221.648,\ nm}$ emission line. Up to now no visible degeneration of the combustion tube was observed.

2.4.9 ICP operation at reduced RF power

The introduction of organic solvent aerosols into the ICP almost always requires elevated RF generator power levels to avoid the extinction of the plasma. Often the highest available generator power level is selected placing significant electrical and thermal stress on the components of the power oscillator and the accompanying power supply. This gives rise to higher wear of these costly components and consequently it is desirable to operate the ICP well below the RF generator upper power limit while still being able to analyze even very volatile samples.

A typical power level for aqueous samples analyzed on the used ICP-OES is 1400 W. At this level the outer gas flow can be reduced to 12 L min^{-1}. All other conditions remained as stated in Table 2.2.

A 10 mg kg^{-1} solution of Ag, Ba, Cd, Cr, Fe, La, Li, Mg, Ni, Pb, Y, Zn and Zr in dichloromethane and a dichloromethane blank were analyzed at 1650 W and at 1400 W. In order to discriminate between effects caused by the aerosol treatment (combustion, CO_2 and O_2 removal) and non-spectroscopic interferences in the plasma, an aqueous standard containing

10 mg kg^{-1} of all analytes was nebulized without the combustion oven and the membrane desolvator installed. Signals of the aqueous standard were also acquired at both power levels.

The effect of the reduced RF generator power for dichloromethane and water as solvents is shown in Figure 2.11. The signals obtained at 1650 W were divided by the signals recorded at 1400 W for each investigated emission line. Those quotients represent signal suppression factors for the comparison of the two power levels.

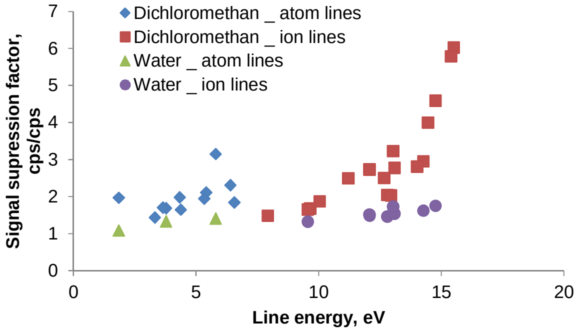

Figure 2.11: Signal suppression caused by the reduction of RF power from 1650 W to 1400 W for emission lines of Ag, Ba, Cd, Cr, Fe, La, Li, Mg, Ni, Pb, Y, Zn and Zr in dichloromethane and water as solvents. The signal suppression factor was calculated by dividing the respective signal obtained at 1650 W by the signal recorded at 1400 W. Aqueous solutions were analyzed without combustion oven and membrane desolvator installed in the aerosol path. Moreover, no oxygen was admixed to the aqueous aerosol. Line energies taken from [15]; error bars not plotted for clarity–RSDs were between 3 and 5 % for all investigated lines.

As shown in Figure 2.11, a reduction of the RF power resulted in a signal suppression of all investigated emission lines when using dichloromethane. Whereas for atom lines the suppression factor was about 2, ion lines showed a clear increase of the suppression factor with increasing total line energy (ionization potential + excitation potential): for Ba (II) $_{455.404,\ \mathrm{nm}}$ (7.93 eV total line energy) a suppression factor of 1.5 was recorded, whereas for the Zn (II) $_{202.548,\ \mathrm{nm}}$ (15.51 eV total line energy) emission line a factor of 6 was determined. This behavior can be attributed to non-spectroscopic interferences in the ICP caused by the presence of molecular gasses (remaining oxygen and carbon dioxide). It is well known, that this matrix effect influences ion lines more than atom lines [21] and the magnitude does correlate with the line energy. The comparatively low suppression factors encountered for aqueous solutions (30-60 % for the ion lines) further support this theory.

2.5 Conclusions

The proposed sample combustion and carbon dioxide removal approach can be used to quantitatively determine trace metal levels in highly volatile solvents. The removal of most of the carbon from the aerosol prior the introduction into the ICP enables stable plasma operation independent of the introduced solvent.

Even though ICP stability is assured by employing the proposed approach, the application to specific samples can be expected to offer several possibilities of optimization: compared to the introduction of aqueous samples the analytical performance is degraded, mainly due to the presence of about 1 % oxygen in the gas stream and analyte-specific losses in the combustion and desolvation system. It seems reasonable to expect further improvements in the analytical performance by using a combustion tube without glass frit and by optimizing the oxygen removal in the membrane desolvator by either using a second desolvator in series or by employing different membrane types. Another problematic issue is the instability of the peristaltic pump tubes towards various organic solvents. This problem could be overcome by using sequential injection flow injection analysis equipment [22].

In the presented form the sample combustion and carbon dioxide removal system poses several distinctive advantages over other approaches reported in literature. The optimization of the ICP is not constrained by the volatility of the sample but rather by the remaining amount of oxygen in the carrier gas stream. There is no clogging of the desolvator’s membrane by sample constituents or extraction additives which can be encountered when the solvent is not combusted. Within the safe operating constraints of the combustion oven, the sensitivity can be enhanced by increasing the amount of sample introduced into the oven. Moreover, species-depending differences in the analyte volatility will not affect the analyte response, as the sample is combusted.

2.6 References

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Part 3

INVESTIGATION OF THE EFFECT OF CARBON DIOXIDE-LOADING ON THE ANALYTE SIGNAL INTENSITY AND PLASMA ROBUSTNESS

3.1 Introduction

As it is described in Part 1, the direct introduction of organic solvents into the ICP causes various problems such as soot formation on the wall of the torch or even plasma extinction, severe spectral interferences, enhancement in background emission and analyte signal suppression. In order to overcome these problems, as described in Part 2, a novel strategy for the combustion of organic solvents and subsequent CO_2 removal prior to the introduction of gas stream into the ICP was introduced. None of the investigated CO_2-removal devices completely remove the CO_2 and in the best case, using PTFE membrane-based aerosol desolvator, 99 % of CO_2 was removed and the rest of CO_2 was introduced to the plasma. The goal of this part of the work was to investigate the effect of CO_2 on the signal intensity and the plasma robustness.

3.2 Experimental

3.2.1 Instrumentation

The ICP-OES used in this work was CIROS Vision EOP (Spectro, Germany) equipped with a cross flow nebulizer, a Scott type spray chamber and a standard torch (2.5 mm i.d.). Operating conditions are shown in Table 3.1. CO_2 (Biogen C, Linde, Austria) was mixed with the nebulizer gas flow. The flow of the CO_2 as the foreign gas was controlled by an external thermal-based mass flow controller (Mass-Flo 1179, MKS Instruments, Germany).

Table 3.1: Instrumental and operation condition

RF power	1400 W
Coolant flow	12.5 L min^{-1}
Auxilary flow	0.6 L min^{-1}
Nebulizer gas flow	0.3 L min^{-1}
Spectrometer	Paschen-Runge mount with 22 CCD line detectors
RF generator	Huth-Kühn power oscillator
Torch	Standard torch; injector with 2.5 mm i.d.
Spray chamber	Cyclonic
Nebulizer	Mira Mist, Burgener Research, USA
Peristaltic pump tubing	Glass expansion Tygon MH 2075; i.d. 0.64 mm

3.2.2 Reagents

Purified water (18 MΩ cm^{-1}, Barnstead Nanopur, Thermo Fisher Scientific, USA) and high purity nitric acids (HNO_3, Suprapur, Merck, Germany) were used throughout. Standards were prepared from 1000 mg L^{-1} multi element stock solution (Al, Ag, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn) (Roti® Star, Germany) in 5 % HNO_3.

3.3 Results and discussion

3.3.1 Effect of CO_2 concentration on signal intensity of various elements

In this part of the work 1 mg L^{-1} multi elements solution was introduced to the plasma using the routine ICP-OES setup (Table 3.1). The effect of different CO_2 concentration (0.32, 0.64, 0.95, 1.2, 1.5, 1.8, 2.2, 2.5, 2.8, 3.1, 3.4 % v/v) on the signal intensity of various elements was investigated. Further increasing of CO_2 (> 3.4 % v/v) caused plasma extinction. The results indicate that the presence of CO_2 in the nebulizer gas flow affects the emission intensity of investigated lines. Figure 3.1 illustrates the normalized signal intensity values of few selected emission lines (As, Se, Be, Cu, Ti, K). Normalized signal intensity is defined as the resultant signal intensities after blank corrections which were normalized to values obtained in the absence of CO_2. As Figure 3.1 shows, the presence of CO_2 caused marked signal depression (up to 65 %) for those elements with ionization potential (IP) lower than 9 eV (e.g. K, Ti, Cu) whereas the emission intensity of atomic lines with IP in the range of 9-11 eV (e.g. arsenic, selenium and beryllium) is enhanced (up to 42 %). The magnitude of the signal enhancement or suppression is directly correlated to the amount of carbon in the plasma and for organic solvents analysis the amount of the carbon depends on the type of the solvent. During the introduction of organic solvents to the developed combustion system, different solvents are expected to produce different amount of CO_2 in the combustion oven and at a given removal efficiency of the membrane desolvator different CO_2 levels in the final gas flow that enters the ICP. This means if we have suppression or enhancement depending on CO_2 concentration there will be a systematic error when the calibration solution does not contain the same solvent as the sample. For the analysis of solvents this is not a significant problem but for the unknown samples this is a limitation because of different behavior of every emission lines in term of enhancement or suppression. Therefore, the use of internal standard cannot be successful, too.

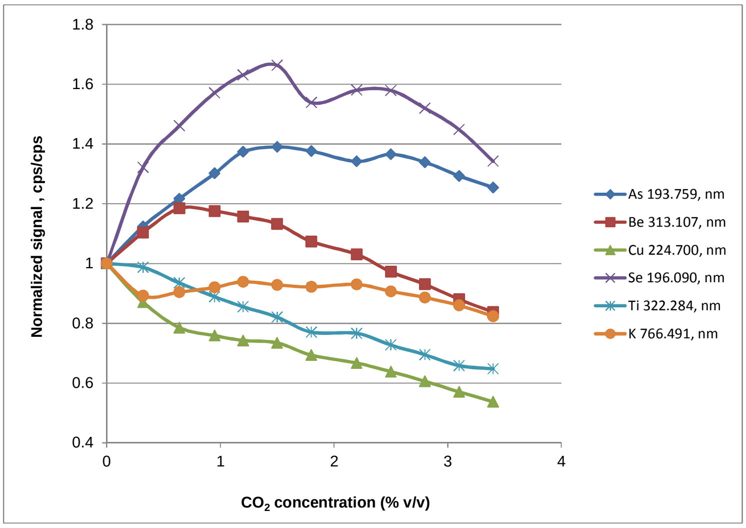

Figure 3.1: Normalized signal (all signal intensities were normalized to 0 % v/v CO_2) versus CO_2 concentration for the selected elements. Elements with IP in the range of 9-11eV (As (IP: 9.84 eV), Be (IP: 9.34 eV) and Se (IP: 9.78 eV) and elements with IP < 9 eV (K (IP: 4.34 eV), Ti (IP: 6.84 eV) and Cu (IP: 7.74 eV). Error bars are smaller than the data points.

3.3.2 Effect of CO_2 concentration on plasma robustness

In this part of our study the variation of the plasma robustness expressed as the Mg (II) $_{280.2,\ nm}$/Mg (I) $_{285.2,\ nm}$ ratio as a function of the CO_2 concentration in the nebulizer gas flow was investigated. The experimental procedure for the plasma robustness determination was as follows: 1 mg L^{-1} solution of Mg was aspirated, CO_2 was added to the nebulizer gas flow in the range of 0- 3.4 % v/v and the Mg intensities at 280.2, nm and 285.2, nm were monitored at each CO_2 concentration. After background correction, the correlation between Mg intensity ratio and CO_2 concentration was plotted (Figure 3.2). As Figure 3.2 displayes, addition of CO_2 to nebulizer gas flow initially caused Mg ratio enhancement and then reaching the maximum level of 9.66 at 0.64 % v/v CO_2. This low amount of CO_2 (< 0.64 % v/v) led to brighter plasma. The enhancement can be related to the increased thermal conductivity between the plasma core and the analyte channel of the ICP discharge caused by the CO_2. With further addition of CO_2 to the nebulizer gas flow a decreasing trend was observed and Mg ratio dropped to the amount of 7.30 at 3.42 % v/v CO_2. The maximum plasma tolerance was 3.42 % v/v CO_2; therefore further investigation of plasma robustness was not possible.

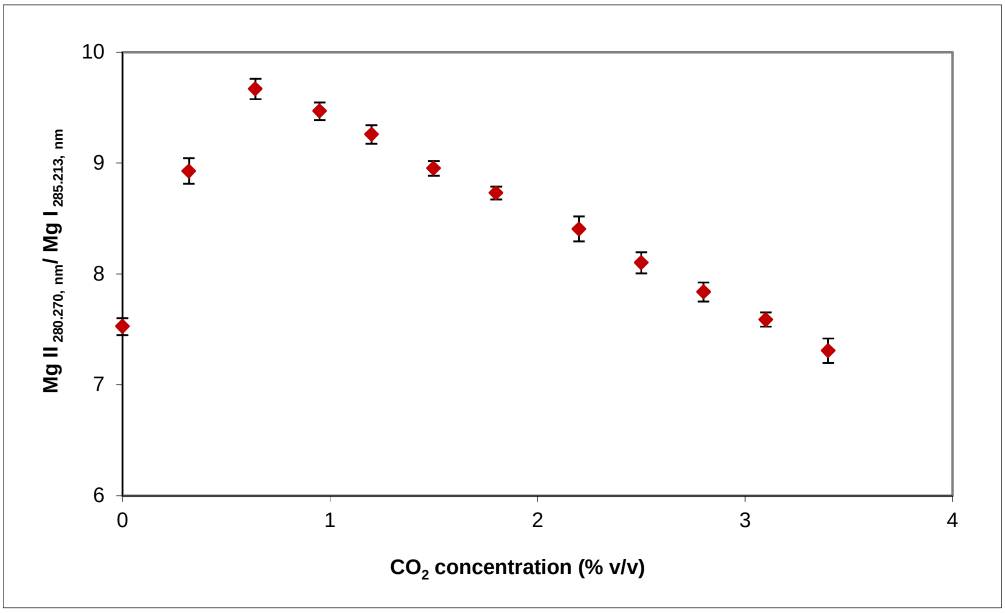

Figure 3.2: Mg (II) $_{280.27,\ nm}$/ Mg (I) $_{285.213,\ nm}$ versus CO_2 concentration (% v/v)

3.4 Conclusions

The results showed that the presence of CO_2 induces a signal enhancement for elements with ionization potential higher than 9 eV. For these elements an increase in signal intensity of up to a factor of 2 was observed at 1.6 % v/v CO_2 in the nebulizer gas flow, while decrease was encountered with further increasing the CO_2 concentration. For elements with ionization potentials lower than 9 eV the signal intensity decreased with increasing CO_2 concentration in the nebulizer gas flow. Moreover, the variation of the plasma robustness expressed as the Mg (II) $_{280.2,\ nm}$/Mg (I) $_{285.2,\ nm}$ ratio as a function of the CO_2 concentration in the nebulizer gas flow was investigated. The plasma robustness first increased from 7.5 to 9.7 when the CO_2 concentration in the nebulizer gas flow was increased from 0 to 0.64 % v/v CO_2 and then decreased linearly to 7.3 at the maximum tested CO_2 concentration of 3.4 % v/v. Further increasing of CO_2 (> 3.4 % v/v) caused plasma extinction.

As the enhancement or suppression of analyte signal is strongly dependent on the CO_2 concentration present, it is important that the CO_2 concentration remains at a constant level during calibration and subsequent analysis of the sample. Therefore, the solvent used for preparing the calibration should match the solvent in the sample. Though this requirement is also a standard procedure for the analysis of aqueous samples (acid matching), it impedes the analysis of samples of unknown organic composition.

Part 4

FUTURE PROSPECTS

I) Improvements in the analytical performance by using a combustion tube without glass frit

II) Further CO_2 and O_2 removal in the membrane desolvator by either using a second desolvator in series or by employing different membrane type

III) Using alternative approaches of suppressing the oxide formation in the oven

IV) Overcoming the non-linear behavior of the calibration function for low concentrations of elements

Part 5

SUMMARY AND CONCLUSION

Direct introduction of organic solvents to ICP-OES causes various problems such as soot formation on the wall of the torch or even plasma extinction, severe spectral interferences, enhancement in background emission and analyte signal suppression. In order to overcome these problems a novel method and instrumrntation for the determination of metal (Ag, Cd, Cr, Fe, La, Li, Mg, Ni, Pb, Y, Zn, and Zr) in volatile organic solvents was developed. In this method, organic aerosol was combusted in a commercial carbon analyzer oven in an oxygen-rich atmosphere and produced carbon dioxide and remaining oxygen were removed from the gas stream prior the introduction into ICP-OES. The proposed combustion/carbon removal approach allowed stable operation of the ICP even when introducing highly volatile solvents that otherwise would have immediately extinguished the plasma.

To remove the CO_2 and O_2, three means of treating the aerosol that left the oven were investigated: falling-film column, hollow fiber gas separation device and the PTFE membrane-based desolvator. Falling-film column is not capable of removing oxygen residues from the combusted aerosol while the hollow fiber gas exchange decices and PTFE membrane-based desolvator are capable of removing both CO_2 and excess O_2 by diffusion. Water condensation is the unifying problem of both the falling-film column and the hollow fiber gas separation device. In contrast, this problem is circumvented in PTFE membrane by heating the membrane wall above 100 ºC. The highest CO_2 removal efficiency was achieved by means of PTFE membrane-based desolvation unit. The non-removable CO_2 causes a signal enhancement for elements with ionization potential higher than 9 eV and suppression for elements with ionization potential lower than 9 eV.

After aerosol treatment in the oven and PTFE membrane, quantification of metals in volatile organic solvents such as acetone, methyl isobutyl ketone, chloroform, dichloromethane, tetrachloroethane or trichloro-trifluoroethane by means of ICP-OES illustrated that halogens act as a realizing reagent for most of the metals. Analyte signals in halogenated solvents were found to be significantly higher than in non-halogenated ones. Thought a stable operation of the plasma was possible, the analyte signal intensities obtained in water were, depending on the element and the solvent, higher than in halogenated solvents.

In this approach the sample combustion and carbon dioxide removal system poses several distinctive advantages over other approaches reported in literature. The optimization of the ICP is not constrained by the volatility of the sample but rather by the remaining amount of oxygen in the carrier gas stream. There is no clogging of the desolvator's membrane by sample constituents or extraction additives which can be encountered when the solvent is not combusted. Within the safe operating constraints of the combustion oven, the sensitivity can be enhanced by increasing the amount of sample introduced into the oven. Moreover, species-depending differences in the analyte volatility will not affect the analyte response, as the sample is combusted.

Part 6

APPENDIX

A ABBREVIATIONS

ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
MDL	Method Detection Limit
MIBK	Methyl Isobutyl Ketone
MO	Metal oxide
MS	Mass Spectrometry
OES	Optical Emission Spectrometry
PTFE	Polytetrafluoroethylene
RF	Radio Frequency
RSD	Relative Standard Deviation

B LIST OF THE SELECTED EMISSION LINES FOR FIGURE 2.3

Ag 328.068, nm	Mn 259.373, nm	V 292.464, nm
Ca 393.366, nm	Mn 257.611, nm	V 311.071, nm
Ca 396.847, nm	Mn 403.076, nm	Zn 213.856, nm
Ca 422.673, nm	Mo 202.030, nm	Ag 338.289, nm
Cd 226.502, nm	Na 588.995, nm	Al 167.078, nm
Cd 228.802, nm	Na 589.592, nm	Al 396.152, nm
Cd 361.051, nm	Ni 221.648, nm	Ar 404.442, nm
Co 228.616, nm	Ni 231.604, nm	Ar 430.010, nm
Co 238.892, nm	Ni 232.003, nm	As 189.042, nm
Cr 205.552, nm	Ni 300.249, nm	B 249.773, nm
Cr 267.716, nm	Pb 220.353, nm	Ba 233.527, nm
Cu 324.754, nm	Pb 283.305, nm	Ba 455.404, nm
Cu 327.396, nm	Pb 405.778, nm	Be 234.861, nm
Fe 238.204, nm	Sb 206.833, nm	Be 313.042, nm
Fe 259.941, nm	Sb 217.581, nm	Bi 223.061, nm
Fe 373.486, nm	Se 196.090, nm	
K 766.491, nm	Sr 407.771, nm	
Li 460.289, nm	Sr 421.552, nm	
Li 670.780, nm	Sr 460.733, nm	
Mg 279.553, nm	Ti 334.187, nm	
Mg 280.270, nm	Ti 334.941, nm	

C LIST OF FIGURES

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D LIST OF TABLES

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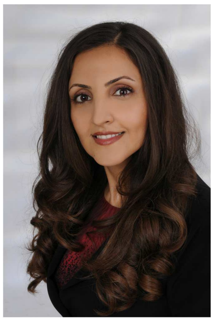
E CURRICULUM VITAE



FARZANEH MORADI

Annenstrasse 7, A-8020 Graz
Email: farzaneh.moradi@hotmail.com
Date of Birth: 21.09.1980

EDUCATION

11/2010-10/2014: **Graz University of Technology** **Graz (AT)**
Ph.D. Analytical Chemistry
Institute of Analytical Chemistry and Food Chemistry
Supervisors: Prof. Dr. Günter Knapp and Dr. Helmar Wiltsche
Development of a novel method and instrumentation for the analysis of volatile organic substances by ICP-OES

10/2003-09/2005: **Lorestan University** **Khoramabad (IR)**
M.Sc. Analytical Chemistry
Chemistry Department
Supervisor: Prof. Dr. Alireza Ghiasvand
Determination of different elements by F-AAS and GF-AAS in a microdroplet formed from a homogeneous liquid-liquid extraction system

09/1999-09/2003: **Bu-Ali Sina University** **Hamadan (IR)**
B.Sc. Chemistry
Chemistry Department

WORK EXPERIENCE

11/2014-12/2014: **Massachusetts Institute of Technology** **Cambridge (USA)**
Visiting *Scholar*
Department of Earth and Planetary Sciences
Supervisor: Prof. Dr. David McGee

11/2010-10/2014: **Graz University of Technology** **Graz (AT)**
University Assistant
Institute of Analytical Chemistry and Food Chemistry

08/2013-01/2014: **University of Massachusetts Boston** **Boston (USA)**
Visiting *Scholar*
School for the Environment
Supervisor: Prof. Dr. Robyn Hannigan
Imaging and elemental analyses of the growing edge of shells from a commercially important bay scallop shell (Argopecten irradians) using a multi-method approach

08/2009-10/2010: **Bioenergy2020+ GmbH** **Graz (AT)**
Junior Researcher
R&D department
Supervisor: Prof. Dr. Ingwald Obernberger
Characterization of new biomass fuels by thermogravimetric analysis

10/2007-04/2009: **Iran Polymer and Petrochemical Institute** **Tehran (IR)**
Project Manager

10/2005-08/2007: **Fasa Azad University** **Fasa (IR)**
Lecturer, Project Manager

TEACHING EXPERINCE

11/2010-10/2014: **Graz University of Technology** **Graz (AT)**
University Assistant
Institute of Analytical Chemistry and Food Chemistry

08/2013-01/20114: **University of Massachusetts Boston** **Boston (USA)**
Grader
School for the Environment

10/2005-08/2007: **Fasa Azad University** **Fasa (IR)**
Lecturer

- ✓ General Chemistry I & II
- ✓ Analytical Chemistry I & II

AWARDS

- ✓ KUWI Scholarship, Graz University of Technology, Graz, **Austria**, 2014
- ✓ First Place Poster Award, 2014 Winter Plasma Conference, Amelia Island, Florida, **USA**, 2014
- ✓ Student Travel Stipend, 2014 Winter Plasma Conference, Amelia Island, Florida, **USA**, 2014
- ✓ Marshall Plan Scholarship, Graz University of Technology, Graz, **Austria**, 2013
- ✓ 8th March Mobility Grant for Outstanding Researcher, Graz University of Technology, Graz, **Austria**, 2013
- ✓ First Place Poster Award, 12th Rio Symposium on Atomic Spectrometry, Foz do Iguacu, **Brazil**, 2012
- ✓ 8th March Mobility Grant for Outstanding Researcher, Graz University of Technology, Graz, **Austria**, 2012
- ✓ Outstanding Research by a Graduate Student Award, Lorestan University, Khoramabad, **Iran**, 2005

Certificate

07/2013-08/2013: **Teaching in English** **Graz (AT)**
Graz University of Technology

COMPUTER SYSTEM SKILLS

- ✓ Microsoft Office Package (Advanced)
- ✓ Chem. Draw
- ✓ Chemical database (SCI Finder)
- ✓ Inkscape

INTERESTS

- ✓ Sport (Hiking, Biking, Table Tennis, Tennis)
- ✓ Dancing
- ✓ Travelling
- ✓ Reading Books

JOURNAL PUBLICATIONS

6 Online combustion followed by carbon dioxide removal: evaluation of a new approach for the analysis of volatile organic substances by inductively coupled plasma optical emission spectrometry
H. Wiltsche*, **F. Moradi,** P. Tirk, G. Knapp
Journal of Analytical Atomic Spectrometry, 2014, 29, 1767
(Selected for the cover photo of the journal)

5 Imaging and elemental analyses of the growing edge of shells from a commercially important bay scallop shell (Argopecten irradians) using a multi-method approach
F.Moradi, H. Wiltsche, G. Knapp, R. Hannigan*
Analytical and Bioanalytical Chemistry, under preparation

4 Evaluation of the Oscillator Frequency of a Free Running RF Generator as a Diagnostic Tool for Inductively Coupled Plasma-Optical Emission Spectrometry
H. Wiltsche*, **F. Moradi**, G. Knapp
Spectrochimica Acta Part B: Atomic Spectroscopy, 2012, 71, 48

3 Electrochemical Synthesis of 6-Amino-5-(3, 4-dihydroxyphenyl) Pyrimidine
S. S. H. Davarani*, N. S. Fumani, H. Arvin-Nezhad, **F. Moradi**
Tetrahedron Letters 2008, 49, 710

2 Selective Homogeneous Liquid-Liquid Extraction and Preconcentration of Thallium Using a new Calix [4] Pyrrole
A. R. Ghiasvand*, **F. Moradi,** H. Sharghi, A. R. Hasaninejad
Asian Journal of Chemistry, 2006, 18, 2016

1 Determination of Silver (I) by Electrothermal-AAS in a Microdroplet Formed from a Homogeneous Liquid-Liquid Extraction System Using Tetraspirocyclohexylcalix[4]pyrroles
A. R. Ghiasvand*, **F. Moradi,** H. Sharghi, A. R. Hasaninejad
Analytical Sciences, 2005, 21, 378

PRESENTATIONS

8 Combustion of Volatile Organic Samples and Consequent CO_2 Removal Prior to Introduction to ICP-OES
*2014 Winter Conference on Plasma Spectrochemistry, Amelia Island, FL, **USA**, January 6-11, 2014*

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