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Alessandra Schneider Henn

DEVELOPMENT OF METHODS FOR Mg, Sr AND Pb ISOTOPIC ANALYSIS OF CRUDE OIL BY MC-ICP-MS

Santa Maria, RS
2021

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Thesis presented to the Graduate Program in Chemistry from Federal University of Santa Maria (UFSM, RS), as a partial requisite to obtain the degree of **Doctor of Science**.

Advisor: Prof. Dr. Érico Marlon de Moraes Flores

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ABSTRACT

DEVELOPMENT OF METHODS FOR Mg, Sr AND Pb ISOTOPIC ANALYSIS OF CRUDE OIL BY MC-ICP-MS

AUTHOR: Alessandra Schneider Henn
ADVISOR: Prof. Dr. Érico Marlon de Moraes Flores

In this work, the determination of isotope ratios of Mg, Sr and Pb in crude oil by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) was performed. Two sample preparation methods were evaluated: (*i*) microwave-assisted wet digestion with a pressurized digestion cavity (MAWD-PDC); and (*ii*) solubilization of inorganic solids after the ASTM D4807 test method. Using MAWD-PDC, up to 0.5 g of crude oil was efficiently digested using just 6 mL of 14.4 mol L^{-1} HNO_3 (75 min, temperature up to 250 °C). MAWD-PDC was shown to be a suitable sample preparation method for subsequent determination of Mg, Sr and Pb concentration and their isotope ratios. On the other hand, the ASTM based method does not require any sophisticated equipment or the use of halogenated solvents. With this method up to 10 g of oil can be dissolved in toluene and filtered through a nylon membrane. Elements present as inorganic solids, such as Mg and Sr, are retained on the nylon membrane and can be easily recovered in water. However, Pb was not recovered using this method, possibly because this analyte is present in crude oil as organic complexes that are not retained on the membrane. Four isolation protocols using column chromatography were evaluated for Mg, Sr and Pb isolation from crude oil matrix. For Mg, isolation was successfully carried out using the cation exchange resin AG 50W-X8. The isolation of Sr and Pb was performed using a sequential isolation protocol relying on the use of the Sr-spec resin. Both isolation protocols were characterized by quantitative yields and matrix elements removal. No statistical difference was observed between the results for Mg and Sr isotope ratios obtained using both sample preparation methods (MAWD-PDC and solubilization). Thus, both sample preparation methods can be used for Mg and Sr isotopic analysis of crude oil. The Mg-Sr-Pb isotopic composition of the Brazilian crude oils evaluated in this work was within the range observed for seawater and the deposit bedrock. The methods developed in this work can be considered as promising tools to decipher the formation history of oil reservoirs.

Keywords: Crude oil. Isotopic analysis. MC-ICP-MS. Magnesium determination. Lead determination. Strontium determination.

RESUMO

DESENVOLVIMENTO DE MÉTODOS PARA ANÁLISE ISOTÓPICA DE Mg, Sr E Pb DE PETRÓLEO POR MC-ICP-MS

AUTORA: Alessandra Schneider Henn
ORIENTADOR: Prof. Dr. Érico Marlon de Moraes Flores

Neste trabalho, foi feita a determinação das razões isotópicas de Mg, Sr e Pb em petróleo por espectrometria de massa com plasma indutivamente acoplado e multi-coletor (MC-ICP-MS). Dois métodos de preparo de amostra foram avaliados: (*i*) digestão por via úmida assistida por micro-ondas com cavidade de digestão pressurizada (MAWD-PDC) e (*ii*) solubilização de sólidos inorgânicos após a norma ASTM D4807. Usando a MAWD-PDC, até 0,5 g de petróleo foram eficientemente digeridos usando apenas 6 mL de HNO_3 14,4 mol L^{-1} (75 min, temperatura de até 250 ° C). A MAWD-PDC mostrou ser um método de preparo de amostras adequado para a subsequente determinação da concentração e das razões isotópicas de Mg, Sr e Pb. Por outro lado, o método baseado na ASTM não requer nenhum equipamento sofisticado ou o uso de solventes halogenados. Com este método, até 10 g de petróleo podem ser dissolvidos em tolueno e filtrados através de uma membrana de nylon. Elementos presentes na forma de sólidos inorgânicos, como Mg e Sr, são retidos nessa membrana e podem ser facilmente recuperados em água. No entanto, Pb não foi recuperado usando esse método, possivelmente porque ele está presente no petróleo na forma de complexos orgânicos que não ficam retidos na membrana. Quatro procedimentos de isolamento usando cromatografia em coluna foram avaliados para o isolamento de Mg, Sr e Pb da matriz do petróleo. Para o Mg, o isolamento foi realizado usando a resina de troca catiônica AG 50W-X8. O isolamento de Sr e Pb foi feito utilizando um protocolo de isolamento sequencial com base no uso da resina Sr-spec. Ambos os protocolos de isolamento foram caracterizados por rendimentos quantitativos e remoção de elementos da matriz. Não foi observada diferença estatística significativa entre os resultados para as razões isotópicas de Mg e Sr obtidos usando ambos os métodos de preparo de amostra (MAWD-PDC e solubilização). Assim, os dois métodos de preparo de amostra podem ser usados para análise isotópica de Mg e Sr em petróleo. A composição isotópica Mg-Sr-Pb dos petróleos brasileiros avaliados neste trabalho está dentro da faixa observada para a água do mar e o leito rochoso do depósito. Os métodos desenvolvidos neste trabalho podem ser considerados ferramentas promissoras para decifrar a história de formação de reservatórios de petróleo.

Palavras-chave: Petróleo. Análise isotópica. MC-ICP-MS. Determinação de magnésio. Determinação de chumbo. Determinação de estrôncio.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BAM	Federal Institute for Materials Research and Testing, from German, Bundesanstalt für Materialforschung und -prüfung
CRM	Certified reference material
FAAS	Flame atomic absorption spectrometry
GC-MC-ICP-MS	Gas chromatography multi-collector inductively coupled plasma-mass spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HEPA	High efficiency particulate air
HPA	High pressure asher
HR	High resolution
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-QQQ-MS	Triple quadrupole inductively coupled plasma-mass spectrometry
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
k’	Capacity factor
LOD	Limit of detection
LOQ	Limit of quantification
LR	Low resolution
MAWD	Microwave-assisted wet digestion
MAWD-PDC	Microwave-assisted wet digestion with a pressurized digestion cavity
MAWD-SRC	Microwave-assisted wet digestion with a single reaction chamber
MAWD-UV	Microwave-assisted ultraviolet digestion
MC-ICP-MS	Multi-collector inductively coupled plasma-mass spectrometry
MIC	Microwave-induced combustion
MR	Medium resolution
NIST	National Institute of Standards and Technology
PDC	Pressurized digestion cavity

PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
REE	Rare earth element
SF	Sector field
SF-ICP-MS	Sector field inductively coupled plasma-mass spectrometry
SRC	Single reaction chamber
SRM	Standard reference material
SSB	Sample-standard bracketing
TIMS	Thermal ionization mass spectrometry
TOF	Time of flight
USAE	Ultrasound-assisted extraction
USN-ICP-MS	Ultrasonic nebulizer inductively coupled plasma-mass spectrometry

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1 INTRODUCTION

Crude oil is a complex mixture of hydrocarbons, usually in a liquid state, which can contain compounds of sulfur, nitrogen and oxygen, in addition to metals and other elements.[1] Variations in the composition and characteristics of crude oil can be observed in relation to viscosity, density, N and S content, level of acids, metals, asphaltenes and resins, among others, which make crude oil a very complex matrix.[2,3] The presence of high levels of aromatic hydrocarbons in combination with asphaltenes and resins can increase the stability of crude oil, which can impair the sample decomposition step. Regarding the presence of metals in crude oil, these can be in the oil in the form of inorganic salts (chlorides and/or sulfates of Ca, K, Mg and Na) and/or as organometallic compounds, mainly associated with porphyrins (Cu, Ni, V, among others) or present in the fractions of asphaltenes and resins.[2-4]

Information related to the geological formation processes, degree of evolution of certain fluids and rocks, origin, type and migration of crude oil can be obtained by the isotopic composition of certain elements in crude oil.[5] The knowledge of the isotopic composition of elements containing a daughter nuclide(s) formed by the decay of naturally occurring radionuclides can be used to establish a correlation between the oil and the source rock, and this information can be useful in crude oil exploration activities.[6,7] Other elements show natural variation in their isotopic composition due to isotope fractionation associated to the geological processes involved and provide information on the conditions under which these proceeded. Thus, the isotopic composition of several elements can be used as a fingerprint for crude oil provenance. The radiogenic decay couples ^{187}Re-^{187}Os and ^{147}Sm-^{143}Nd, as well as isotope ratios of transition metals, such as V, Ni, and Mo, have recently been used as proxies of petrogenesis of hydrocarbon reservoirs.[5-7] Traditionally, carbon, hydrogen, nitrogen, and sulfur isotopic compositions are measured in crude oil for this purpose. However, these elements are rarely associated to the source rocks of crude oil reservoirs. Hence, in order to better establish the relationship between oil and source rocks, the development of methodologies for novel “isotopic tools” in crude oil geochemistry is of extreme relevance.[5]

Elements such as Mg, Sr and Pb have been used as isotopic tracers in geochemical, environmental and/or biomedical sciences. The isotopic analysis of Mg, Sr and Pb has been performed in several matrices, which include environmental samples,[8,9] geological and archeological materials,[10-12] biological fluids and tissues.[13,14] However, only few works were found in the literature on Pb isotopic composition of crude oil, and only a single work was found for Sr.[15-20] Moreover, no papers have reported Mg isotopic analysis of crude oil so far. As a result, information on the isotopic composition of these elements in crude oil is still lacking, hampering their potential use as geochronometers and/or proxies.

Multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) is the technique frequently used for high-precision isotope ratio measurements.[21] However, it requires chemical isolation of the target element prior to analysis in order to minimize matrix effects and spectral interferences. The most commonly used approach for chemical isolation is column chromatography by means of an ion exchange or extraction resin.[10,11,13] However, before analyte isolation, crude oil samples have to be efficiently digested. In this sense, a major challenge in crude oil analysis is the sample decomposition step, as an efficient decomposition of the crude oil matrix is difficult to be achieved.[22,23] Most of the works so far rely on the use of conventional sample preparation methods, such as acid digestion followed by dry ashing,[20] liquid-liquid extraction[16,17] or high-pressure asher digestion.[18,19] These methods can be time-consuming and use large amounts of concentrated reagents, which may affect the blank levels. This challenge is even more difficult if medium or heavy crude oils (API < 31.1) must be analyzed, which present a highly stable matrix, due to stable carbon-based compounds and the presence of aromatic compounds.[3,22] In order to overcome these limitations, methods using microwave radiation have been used for acid digestion of crude oils for their subsequent elemental determination using a variety of analytical techniques.[22]

As an alternative, ultra-high pressure systems, such as the single reaction chamber system[24] (SRC, UltraWAVE™, Milestone, Italy) and the pressurized digestion cavity[25] system (PDC, Multiwave 7000, Anton Paar, Austria), allow higher digestion temperatures and pressures (up to 300 °C and 199 bar for both equipment)[24,25] than conventional systems, thus assuring a more efficient digestion. In recent works, these systems have been successfully applied to the digestion of several complex matrices,[26-31] including crude oil,[32] for the subsequent metal and metalloid determination. It was shown possible to digest a relatively high sample mass (up to 1 g of heavy crude oil) achieving low values of residual carbon and residual acidity, making the digests compatible with analysis using plasma-based techniques.[32]

In this way, the goal of the present work was to develop methods for Mg, Sr and Pb isotopic analysis of crude oil using high-precision MC-ICP-MS to provide analytical tools for crude oil provenancing. Microwave-assisted wet digestion with a pressurized digestion cavity (MAWD-PDC) and, alternately, a method based on the solubilization of inorganic solids obtained after the ASTM D4807 test method (Standard Test Method for Sediment in Crude Oil by Membrane Filtration from the American Society for Testing and Materials)[33] were evaluated and applied as crude oil sample preparation methods. Special attention was paid to fine-tuning the column chromatography isolation protocols, rendering them suited for the sample solution matrices as obtained upon crude oil decomposition.

2 LITERATURE REVIEW

This literature review is divided in two parts. First, the general aspects of crude oil will be addressed, as well as those related to the Mg, Sr and Pb isotopic analysis of crude oil. In the second part, different approaches used for crude oil decomposition involving digestion, combustion and extraction methods will be presented and discussed. Moreover, important aspects of chemical isolation procedures for isotopic analysis will be addressed, as well as the principles of ICP-MS and MC-ICP-MS. Spectral interferences, matrix effects and instrumental mass discrimination will also be presented.

2.1 CRUDE OIL

Crude oil is a mixture of naturally occurring hydrocarbons, usually in a liquid state. This mixture can contain sulfur-, nitrogen- and oxygen-containing compounds, resins and asphaltenes, in addition to some metals and other trace elements.[1,3] The most accepted theory about the origin of crude oil establishes that it is originated from the decomposition of organic matter by the combined action of temperature, pressure and time, inside sedimentary source rocks. After its formation, crude oil migrates to sedimentary reservoir rocks, where it is usually found beneath the Earth's surface.[3]

2.1.1 Chemical composition

The physical characteristics of crude oil can vary with the location and age of the oil reservoir, as well as with the depth of the reservoir.[3,34] Indeed, crude oils with very different characteristics can be produced by two adjacent reservoirs. This variation is due to the different proportion of chemical compounds present in crude oil, which can be divided in two major classes: hydrocarbons (paraffinic, naphthenic and aromatic hydrocarbons) and non-hydrocarbons (sulfur, nitrogen and oxygen containing compounds, resins, asphaltenes, and metals).[2,3,34]

The hydrocarbon content of petroleum can be as high as 97% by weight.[3,34] The presence of paraffins usually decreases with the increase of molecular weight or boiling temperature of crude oil fractions. Naphthenic hydrocarbons can be present in all fractions of crude oil and can compose up to 60% of the total hydrocarbons. Fractions with higher molecular weight or boiling point have, in general, higher aromatic hydrocarbons content.[2,3,35,36] However, most aromatic hydrocarbons also contain paraffinic chains and naphthenic rings in their structure.[3]

Although the concentration of sulfur, nitrogen and oxygen compounds may be relatively low in some crude oil fractions (as they tend to concentrate in higher-boiling point fractions), their presence causes some concern in the refining process.[3] The presence of these compounds can compromise the characteristics of final products, leading to discoloration and/or instability during storage.[2,3,35] Additionally, catalyst poisoning and corrosion are also noticeable effects during the refining process, when these compounds are present.[2,35]

Metals can be present in crude oil as inorganic water-soluble salts, as chlorides and/or sulfates (for example, Ca, K, Mg and Na).[2,3] Other metals can be present in the form of oil-soluble organometallic compounds (for example, Cu, Ni and V).[3,4] The occurrence of metals in crude oil is of great importance to the petroleum industry. Metals such as Ni and V can poison catalysts used for sulfur and nitrogen removal, as well as modify the activity of catalysts during the catalytic cracking process.[35,36] In addition, elements such as Ca, K, Mg, Na, and Sr may also cause several problems such as fouling or corrosion of equipment. In this sense, several countries have implemented regulations to establish limiting concentrations for these elements in crude oil.[35,37]

Asphaltenes and resins are polar molecules often containing heteroatoms such as sulfur, nitrogen or oxygen. These substances have similar molecular structures, formed by condensed aromatic rings linked to naphthenic rings (up to 20 rings) and paraffinic side chains.[3] However, asphaltenes differ from resins due to their larger size. These fractions are the main constituents of asphalt and heavy fuel oils.[2]

Despite the wide variation in chemical composition and physical properties, the elemental composition of crude oil varies over narrow limits, as can be observed in Table 1. Since crude oil is basically formed by carbon and hydrogen, the proportion between these two elements is practically constant for different types of oil. Thus, it is not possible to classify crude oil in terms of the carbon content in the same way in which coal is classified for example. Therefore, other methods are used for crude oil classification.[3,37]

Table 1. Crude oil elemental composition (adapted from Brasil *et al.*[37]).

Element	% by weight
Carbon	83 to 87
Hydrogen	10 to 14
Nitrogen	0.1 to 2
Oxygen	0.05 to 1.5
Sulfur	0.05 to 6
Metals	<0.3

2.1.2 Classification

The classification of crude oil oils can be performed according to their physical characteristics and chemical composition.[3] The most usual classification is related to crude oil density performed according to the American Petroleum Institute gravity (API gravity). The API gravity is a measure of how heavy or light a crude oil is compared to water and can be calculated with the equation below:

$$°API = \frac{141.5}{d_{15.6/15.6}} - 131.5 \quad (1)$$

where $d_{15.6/15.6}$ is the ratio between the density of the oil at 15.6 °C and the density of water at the same temperature.[3]

Based on the API gravity it is possible to classify crude oils as light (API gravity higher than 31.1), medium (API gravity from 22.3 to 31.1), heavy (API gravity from 10 to 22.3), extra heavy (API gravity below 10).[3,34] Light crude oils are liquid at room temperature, have low viscosity and flow freely, as they present a high content of paraffinic hydrocarbons. Heavy and extra heavy crude oils have high viscosity, being almost solid at room temperature. Generally, those types of crude oil present a higher content of asphaltenes, resins, sulfur and nitrogen compounds, as well as metals.[34,37]

2.2 ISOTOPIC ANALYSIS OF CRUDE OIL

The isotopic composition of certain elements in crude oil can be used to obtain information related to the geological formation processes, degree of evolution of certain fluids and rocks, origin, type and migration of crude oil.[5] Information on the isotopic composition of radiogenic nuclides, formed by the decay of radioactive nuclei (e.g., ^{87}Sr formed by the decay of ^{87}Rb), can be used to establish a link between the oil and the source rock, and this knowledge can be useful in crude oil exploration activities.[6,7] Other elements show natural variation in their isotopic composition due to isotope fractionation during the geological processes and can provide information on the conditions under which these occurred.

Isotopic compositions of several elements have been used as a fingerprint for crude oil provenance. The radiogenic decay couples ^{187}Re-^{187}Os and ^{147}Sm-^{143}Nd, as well as isotope ratios of transition metals commonly found in crude oil associated to organometallic compounds, such as V, Ni, and Mo, have recently been used for this purpose.[5-7] In addition, the isotopic compositions of carbon, hydrogen, nitrogen, and sulfur are traditionally determined in crude oil to obtain information about its source, maturity, and age.[38-40] However, these elements are rarely associated to the source rocks of crude oil reservoirs. Hence, in order to better establish the relationship between oil and source rocks, the development of methodologies is of extreme relevance in crude oil geochemistry.

Elements such as Mg, Sr and Pb have been used as isotopic tracers in environmental, geochemical and biomedical applications. The isotopic analysis of Mg, Sr and Pb has been performed in several matrices, such as environmental samples,[8,9] geological and archeological materials,[10-12] biological fluids and tissues,[13] among others. However, only a limited number of works have reported Pb isotopic analysis of crude oil,[16-19] and only a single work was found for Sr.[20] Moreover, no papers have reported Mg isotopic analysis of crude oil so far. As a result, there is still a lack of information about the isotopic composition of these elements in crude oil, hampering their potential use as geochronometers and/or proxies.

The combination of MC-ICP-MS with chemical isolation of the target element is a widely used approach for high-precision Mg, Sr and Pb isotope ratio measurements.[21] However, before isolation, crude oil samples have to be efficiently digested, which, in case of crude oil, is not a simple task, due to the high chemical resistance of the carbonaceous matrix.[22,23]

2.3 CRUDE OIL DECOMPOSTION METHODS

Sample preparation can be considered the most critical step in elemental and/or isotopic analysis. For crude oil, the decomposition step is the major challenge of analysis, as an efficient decomposition of the matrix is not always possible.[22,23] The selection of the decomposition method depends, mainly, on the nature of the sample, the analyte, the concentration of the analyte in the sample, the analytical technique used for the determination, and the required precision and accuracy.[23,41] Additionally, the decomposition method should be simple and fast, require a low volume of reagents, have a high sample throughput, and avoid analyte losses and/or contamination.[41,42] The use of an efficient decomposition method is important in order to obtain digests with low carbon and residual acidity. The presence of high carbon and residual acidity of digests can cause changes in the transport of the analyte to the plasma. Additionally, the presence of high carbon content can cause signal enhancing effects due to charge transfer reactions involving carbon-containing charged species in the plasma.[43-47]

Different approaches have been used for crude oil decomposition, involving wet digestion or combustion methods. Extraction methods, which use less severe conditions for crude oil pretreatment, have also been used in a lesser extent.[22,48] Thus, in this section, crude oil decomposition methods aiming metals determination will be addressed.

2.3.1 Wet digestion

Wet digestion methods are usually performed using concentrated acids under heating. Most wet digestion methods involve the use of nitric acid as an oxidizer of the organic matter or its combination with other reagents such as hydrochloric acid, sulfuric acid, and hydrogen peroxide. The amount of reagents used depend on the sample mass, type of matrix, analyte concentration and determination technique.[23,41,42]

Open or closed systems can be used for wet digestion. However, open systems are more susceptible to systematic errors, such as partial digestion of the sample, contamination, and losses by volatilization.[42] In addition, the maximum temperature of these systems is limited by the boiling point of the acid, which in case of concentrated nitric acid (14 to 16 mol L^{-1}) is around 122 ºC. This temperature is insufficient for the complete digestion of crude oil matrix, which requires higher temperatures for decomposition. On the other hand, decomposition in open systems enables higher sample throughput, and use relatively cheaper equipment and materials.[41,42]

Closed vessels have been used for crude oil digestion to increase the digestion efficiency and to reduce the digestion time.[22,42] In closed vessels, the synergistic effects of temperature and pressure promote the increase of the oxidative power of the acids. Moreover, closed systems are essentially isolated from the laboratory atmosphere, minimizing contamination, and allowing the determination of the analytes at trace levels. Another advantage of closed systems is that they prevent the loss of volatile species that can occur when digestion is performed in open vessels.[41,42]

Pressurized digestion systems, such as the High Pressure Asher^{TM} (HPA), have been proposed with the aim of increasing the maximum temperature reached. In these systems nitric acid can be used alone to digest most organic samples and a digestion temperature of up to 320 °C (pressure of up to 130 bar) can be used. The American Society for Testing and Materials (ASTM)[49] recommends this method for crude oil digestion and further metal and metalloid determination by inductively coupled plasma optical emission spectrometry (ICP-OES) or graphite furnace atomic absorption spectrometry (GFAAS). In this case, up to 700 mg of crude oil can be digested using 5 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl. The system is pressurized with up to 110 bar of argon or nitrogen, and a heating program of 180 min at up to 300 °C is applied.[49] Despite the advantages of HPA digestion, only a few applications of this method can be found in the literature for crude oil digestion.[50,51]

Methods using microwave radiation have been used for acid digestion, allowing a relative fast heating of the sample.[23,41] Several examples of microwave-assisted wet digestion (MAWD) of crude oil samples can be found in the literature.[22,32,50,52-56] In general, the advantages associated to this method are similar to those mentioned for closed systems with conventional heating, such as higher decomposition efficiency, lower risks of analyte losses and contamination, and lower consumption of reagents.[23] Additionally, the possibility of automation, with real-time power, pressure and temperature control are the major advances of MAWD.[23,41,42] However, the maximum pressure of the system limits the sample mass (in general, sample masses up to 500 mg are used).[22]

The combination of MAWD and ultraviolet radiation (known as microwave-assisted ultraviolet digestion, MAWD-UV) was proposed by Florian and Knapp[57] to obtain a high-efficiency digestion of organic matrices. In this method, a UV emission lamp (an electrodeless Cd discharge lamp with main emission line at 228 nm) is inserted into the quartz digestion vessel conventionally used for MAWD, being activated by microwave radiation.[57] This method has been used for the digestion of crude oil and subsequent determination of rare earth elements (REEs).[55] Through MAWD-UV of crude oil, it was possible to digest sample masses up to 500 mg using a mixture of 4 mol L^{-1} HNO_3 and 4 mol L^{-1} H_2O_2. Interferences caused by excessive acid concentration and carbon content in digests were minimized allowing limits of quantification as low as 0.3 ng g^{-1} for REEs.[52] Thus, the advantages of the MAWD-UV method include the possibility of using diluted acids, the lower consumption of reagents and the reduction of residue generation.[23,40] However, the relative low lifetime of the UV emission lamps is a drawback of this method. After several cycles of decomposition, a loss of digestion efficiency has been observed in some cases, resulting in replicates with different visual aspect and residual carbon content.[58]

Despite the several advantages reported about the use of microwave radiation for sample decomposition, the limiting maximum pressure of the equipment, which is usually up to 80 bar, limits the maximum sample mass that can be digested in these systems.[23] In order to overcome this limitation, ultra-high pressure systems, such as the single reaction chamber system[24] (SRC, UltraWAVE™, Milestone, Italy) or the pressurized digestion cavity system[25] (PDC, Multiwave 7000, Anton Paar, Austria), have been developed. These systems allow higher digestion temperatures and pressures than conventional systems (up to 300 °C and 199 bar for both equipment, respectively), thus assuring a more efficient digestion.[24,25] In recent works, these systems have been successfully applied to the digestion of several complex matrices,[26-30] including crude oil,[32,53] for subsequent metal and metalloid determination. It was shown to be possible to digest a relatively high sample mass (up to 1 g of heavy crude oil)[32] achieving low values of residual carbon and residual acidity, making the digests compatible with analysis using plasma-based techniques.

2.3.2 Combustion

Combustion methods have been extensively used for the decomposition of organic samples. Dry ashing using a muffle furnace has probably been the most widely used combustion method.[42] This method is recommended by the ASTM for crude oil digestion and further Fe, Ni, and V determination by flame atomic absorption spectrometry (FAAS).[59] Up to 20 g of crude oil can be digested by heating at 525°C in a muffle furnace, and the resulting ash can be dissolved in a small volume of dilute nitric acid.[59] This method allows pre-concentration of elements in the final solution, which is useful when very low concentrations need to be determined. In addition, other advantages of dry ashing methods are the possibility to decompose high sample masses, reduced reagents consumption, possibility to control the acidity of the final solution, as well as the simplicity of execution. However, the main disadvantages are the long time of decomposition, and the possibility of losses of analytes by volatilization.[23,41,42]

In order to overcome the drawbacks of combustion in open vessels, combustion methods in closed vessels such as the combustion bomb and the oxygen flask (also called Schöniger's flask) were proposed.[42,60,61] In these methods, the sample is combusted inside a closed vessel purged with oxygen, and the analytes are absorbed into a suitable solution. Organic matrices can be digested in a few minutes and very simple and relatively inexpensive equipment are required. However, only one sample can be digested at a time and contamination due to the metallic parts of the combustion bomb can occur.[60]

Alternatively, microwave-induced combustion (MIC) has been proposed with the aim of minimizing the disadvantages of conventional digestion and combustion methods.[23,62] The MIC method combines the advantages of the microwave-assisted wet digestion method with those of the combustion in closed vessels. In this procedure, the sample is placed on a quartz holder device inside a quartz vessel containing an absorbing solution. The vessel is pressurized with oxygen (generally 20 bar) and the ignition step is performed by microwave radiation using a diluted ammonium nitrate solution as igniter. A reflux step can also be performed in order to improve analytes recovery. Among the advantages of the MIC method are the low limits of detection (LODs), low residual carbon content of the digests, the use of relatively high sample masses and the possibility to obtain diluted solutions compatible with different determination techniques.[23,62]

Since its development, the MIC method has been used for the decomposition of hard-to-digest samples, especially those with high carbon content and highly stable structures, such as pitch,[63,64] carbon nanotubes,[65,66] graphite,[67] polymers,[68-70] coal[71,72] and crude oil.[50,56,73] In the case of crude oil, up to 500 mg could be efficiently digested using this method. Crude oil can be placed on the quartz holder device using polycarbonate capsules or by wrapping the samples in a polyethylene film. The addition of crude oil on small pieces of filter paper is also possible. Regarding the absorbing solution, diluted nitric acid solutions were shown to be suitable for recovering metals from crude oil.[50,56,73]

2.3.3 Extraction

Extraction methods use less severe conditions for sample pretreatment and are usually applied when it is necessary to maintain the integrity of a species or compound (e.g. speciation analysis) and/or to assess only the extractable analyte.[42] Through extraction methods it is possible to reduce the use of concentrated reagents, such as acids, commonly used in wet digestion methods. Thus, extraction is generally performed with diluted solutions of acids, alkalis and complexing reagents. Organic solvents were also reported as extraction solvents.[41,42]

Only a few publications have reported the use of extraction methods for crude oil analysis.[74,75] Ultrasound-assisted extraction (USAE) was proposed for the determination of metals in crude oil by ICP-OES. The use of ultrasound allowed quantitative extraction in less time and lower temperature than the wet digestion method. However, concentrated nitric acid was still used as extraction solvent.[75] In another work, a hot solvent extraction method based on ASTM D6470[76] was proposed for Ca, Fe, Mg, Na and Sr determination in crude oil.[74] ASTM D6470 is a standard test method for salt determination in crude oils. In this methodology, crude oil is mixed with xylene, isopropyl alcohol, acetone and water, followed by heating, for the extraction of inorganic salts into the aqueous phase.[76] After extraction, the chloride content in the aqueous phase is determined via potentiometric titration, and the results are expressed as NaCl in crude oil. The modified ASTM method enabled suitable recoveries (from 91 to 120%) for all the analytes.[74]

Another standard test method which shows potential for further metals determination is ASTM D4807,[33] which is recommended for inorganic solids determination in crude oil after membrane filtration. This method involves the solubilization of crude oil in hot toluene (90 °C), subsequent filtration under vacuum through a nylon membrane with 0.45 μm porosity, and final weighing of the membrane containing the retained solids. Elements such as Mg and Sr, present as inorganic solids in crude oil, are retained on the membrane, and can be easily recovered in water. This ASTM method does not require sophisticated equipment and can be an alternative sample preparation for crude oil.[33]

Table 2 shows an overview of crude oil sample preparation methods for further metals determination.

Table 2. Crude oil sample preparation methods for further metals determination.

Analytes	Decomposition method	Technique	LOQ or LOD	Ref.
La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Yb	Wet digestion: 2 g of crude oil were vigorously mixed with 2 mL of H_2O. After centrifuging, the oil phase was digested using 3 mL of concentrated H_2SO_4 followed by the addition of 4 mL of H_2O_2. The resulting colorless aqueous solution was made up to 10 mL with deionized water. Accuracy not informed.	ICP-MS	Not informed	77
As, Ba, Co, Mn, Mo, Ni, Pb and V	HPA digestion: 500 mg of crude oil were digested with 6 mL HNO_3 (65%) and 0.5 mL H_2O_2 (30%). The heating program was: 1 h of ramp to 300 °C, temperature kept for 30 min. Agreement with crude oil reference material values (NIST SRM 1634c) was between 98.6 and 125%.	ICP-MS	Not informed	50
Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Rb, Re, Se, Sr, Ti, U, V and Zn	HPA digestion: 500 mg of crude oil were digested with 6 mL HNO_3 (65%) and 0.5 mL H_2O_2 (30%) at 300 °C and 125 bar for 2 h. Digests were transferred into 50 mL tubes, 0.5 mL of 4% (m/v) HCl was added and made up with water. Agreement with crude oil reference materials values (NIST SRM 1634c and NIST SRM 1084a) was between 92.1 and 110% (except for Ag and Ti which were lower).	ICP-QQQ-MS	LODs ranged from 0.004 (for Re) to 1300 ng g^{-1} (for K)	51
As, Ba, Co, Mn, Mo, Ni, Pb and V	MAWD: 300 mg of crude oil were digested with 7.5 mL of HNO_3 and 0.5 mL of H_2O_2. The heating program was: 600 W for 20 min; 900 W for 25 min (ramp of 15 min). Agreement with crude oil reference material values (NIST SRM 1634c) was between 82.8 and 117%.	ICP-MS	Not informed	50
Fe, Ni and V	MAWD: 300 mg of crude oil were mixed with 6 mL 9.1 mol L^{-1} HNO_3 and 2 mL H_2O_2 (30%) and kept for 10 min at room temperature before digestion. The heating program was: 10 min ramp to 180 °C, temperature kept for 20 min; 10 min ramp to 230 °C, temperature kept for 20 min. Digests were diluted to 20 mL with water. Recoveries for standard addition experiments ranged from 95.0 to 104.2% and no statistical difference was observed between results obtained by MAWD and ASTM D5708 method (dry ashing).	ICP-OES	LOD Fe: 0.01 µg g^{-1} Ni: 0.03 µg g^{-1} V: 0.007 µg g^{-1} LOQ Fe: 0.04 µg g^{-1} Ni: 0.1 µg g^{-1} V: 0.02 µg g^{-1}	54

Table 2. Crude oil sample preparation methods for further metals determination (continued).

Analytes	Decomposition method	Technique	LOQ or LOD	Ref.
Ni and V	MAWD: 100 mg of crude oil were mixed with 3 mL of HNO_3 (65 %) and kept for 30 min at room temperature. Vessels were heated at 180 °C for 20 min. After cooling, 4 mL of H_2O_2 (30%) were added and vessels were heated again for 20 min at 180 °C. Digests were diluted to 15 mL with water. Agreement with crude oil reference material values (NIST SRM 1634c) was 96.4% for Ni and 98.2% for V.	ICP-OES	LOD: Ni: 0.24 µg g^{-1} V: 0.06 µg g^{-1} LOQ: Ni:0.79 µg g^{-1} V: 0.20 µg g^{-1}	52
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb	MAWD-UV: 500 mg of crude oil were weighed inside the quartz vessels used for MAWD. Before crude oil weighing, a PTFE device was transferred to quartz vessels to maintain the UV lamp in the vertical position. Quartz vessels were filled with 10 mL of 4 mol L^{-1} HNO_3 and 4 mol L^{-1} H_2O_2, and UV lamps were positioned inside vessels. The heating program was: 400 W for 10 min (ramp of 10 min); 900 W for 10 min (ramp of 10 min), and 0 W for 20 min (cooling step). After cooling, samples were diluted with water to 25 mL. Recoveries for standard addition experiments ranged from 97 to 102% and no statistical difference was observed between results obtained by MAWD-UV and NAA (for La, Sm, and Yb).	USN-ICP-MS	LOQs ranged from 0.3 ng g^{-1} (for Tb, Tm, Lu) to 2.0 ng g^{-1} (for Ce)	55
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb	MAWD-SRC: 1000 mg of crude oil were weighed inside the quartz digestion vessels and 8 mL of 14.4 mol L^{-1} HNO_3 were added. The PTFE liner from SRC chamber was filled with a mixture of 130 mL of water and 5 mL of HNO_3 (65%), and the chamber was pressurized with 40 bar of argon. The heating program was: 10 min ramp to 80 °C, temperature kept for 10 min; 10 min ramp to 270 °C, temperature kept for 10 min. The digests were diluted with water to 25 mL. Recoveries for standard addition experiments ranged from 94 to 110% and no statistical difference was observed between the results obtained by MAWD-SRC, MAWD and MIC.	USN-ICP-MS	LOQs ranged from 0.1 ng g^{-1} (for Eu, Tb) to 2.0 ng g^{-1} (for Ce)	32

Table 2. Crude oil sample preparation methods for further metals determination (continued).

Analytes	**Decomposition method**	**Technique**	**LOQ or LOD**	**Ref.**
Ba, Ca, K, Mg, Na and Sr	MAWD-SRC: 500 mg of crude oil were digested with 6 mL HNO_3 (65%). The PTFE liner from SRC chamber was filled with a mixture of 130 mL of water and 5 mL of HNO_3 (65%), and the chamber was pressurized with 40 bar of argon. The heating program was: 5 min ramp to 90 °C; 10 min ramp to 110 °C, temperature kept for 5 min; 10 min ramp to 120 °C; 10 min ramp to 130 °C; 20 min ramp to 250 °C, temperature kept for 15 min. The digests were diluted with water to 25 mL. Accuracy not informed.	ICP-OES	Not informed	53
Ni and V	Dry ashing: 5 g of crude oil were placed in 10 mL culture tubes and heated in a muffle at 550 °C for 12 h. After cooling, 4 mL HNO_3 (75%) and 1 mL H_2O_2 (30%) were added to the tubes. Finally, 1 mL HCl (36%) was added to the vessels. Recoveries for standard addition experiments ranged from 90 to 100%.	ICP-MS	LOD Ni: 0.11 ng g^{-1} V: 0.61 ng g^{-1}	78
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb	MIC: 250 mg of crude oil were inserted in polycarbonate capsules. Capsulated samples and a small disc of filter paper, moistened with 50 µL of 6 mol L^{-1} NH_4NO_3, were positioned on a quartz holder that was introduced into the quartz vessel containing 6 mL 3 mol L^{-1} HNO_3 as absorbing solution. After, the vessels were closed, fixed on the rotor and pressurized with 20 bar of oxygen. The heating program was: 1400 W for 5 min and 0 W for 20 min. Resultant solutions were diluted with water to 25 mL. Recoveries for standard addition experiments ranged of 97.8 to 102% and no statistical difference was observed between the results obtained MIC and by NAA (for La, Sm and Yb).	USN-ICP-MS	LOQs ranged from 0.7 ng g^{-1} (for Tb, Ho, Tm) to 5.1 ng g^{-1} (for Ce)	73
Ag, As, Ba, Bi, Ca, Cd, Cr, Fe, K, Mg, Li,Mn, Mo,Ni, Pb, Rb, Se, Sr, Tl, V, and Zn	MIC: 500 of crude oil were wrapped in polyethylene films and placed together with a disc of filter paper on a quartz holder. The paper was moistened with 50 µL of 6 mol L^{-1} NH_4NO_3. The holder was placed inside the quartz vessel containing 6 mL 2 mol L^{-1} HNO_3 as absorbing solution. After closing and capping the rotor, the vessels were pressurized with oxygen at 20 bar. The heating program was: 1400 W for 5 min and 0 W for 20 min. Resultant solutions were diluted with water to 25 mL. Recoveries for standard addition experiments ranged from 97 to 103% and agreement with crude oil reference material values (NIST SRM 1634c) was between 97.2 and 102% (for As, Ba, Ni, Se and V). No statistical difference was observed between the results obtained MIC and by NAA (for As, Cr, Mn and Mo).	ICP-MS ICP-OES	LOQs ranged from 0.002 (for Cd) to 0.4 µg g^{-1} (for K)	56

Table 2. Crude oil sample preparation methods for further metals determination (continued).

Analytes	Decomposition method	Technique	LOQ or LOD	Ref.
As, Ba, Co, Mn, Mo, Ni, Pb and V	MIC: 300 mg of crude oil was added on 2 filter papers placed on the quartz holder. The sample was covered with 2 additional filter papers and moistened with 55 µL of 6 mol L^{-1} NH_4NO_3. The holder was inserted into the vessel containing 3.75 mL HNO_3 (65%), 0.25 mL of H_2O_2 (30%) and 4 mL H_2O. After closing and capping the rotor, the vessels were pressurized with oxygen at 20 bar. The heating program was: 1400 W for 20 min and 0 W for 15 min. Agreement with crude oil reference material values (NIST SRM 1634c) was between 84.4 and 120%.	ICP-MS	Not informed	50
Ca, Fe, Mg, Na and Sr	Extraction: 40 g of crude oil were mixed with 70 mL of xylene and manually agitated. The solution was transferred to an extractor flask and 25 mL isopropyl alcohol and 15 mL acetone were added. The mixture was heated to boiling and after 5 min the heating was stopped and 125 mL heated water (80 °C) were added. The mixture was heated again for 15 min. After cooling and separation into two phases, the aqueous phase was collected for analysis. Recoveries for standard addition experiments ranged from 91 to 120%.	ICP-OES	LOQs Na: 3.29 mg L^{-1} Ca: 0.08 mg L^{-1} Mg: 1.09 µg L^{-1} Sr: 0.20 ng L^{-1} Fe: 0.87 µg L^{-1}	74
Cd, Cr, Fe, Mn, Mo, Ni, Ti, V and Zn	USAE: 200 mg of crude oil were mixed with 0.2 mL of toluene and 15 mL HNO_3 (65%). The mixture was agitated for 2 min in a vortex and then heated at 85 °C for 30 min. After heating, the samples were sonicated in an ultrasonic bath for 15 min. After sonication 10 mL of the aqueous phase was collected for analysis. Agreement with crude oil reference material values (NIST SRM 1634c) was 99% for Ni and 96% for V and agreement with values obtained after MAWD ranged from 89.9% to 105.1%.	ICP-OES	LOQs ranged from 0.008 µg g^{-1} (for Mn) to 0.62 µg g^{-1} (for Zn)	75

2.4 CHEMICAL ISOLATION FOR ISOTOPIC ANALYSIS

Most of the applications for high-precision isotopic analysis using MC-ICP-MS require chemical isolation of the target element.[21] This procedure allows the minimization of matrix effects and spectral interferences (except those originated from plasma constituents). The most used approach for purification is column chromatography by means of an ion exchange or extraction resin. Ion exchange column chromatography is a flexible approach, and is often preferred over other separation methods, such as solvent extraction or sublimation.[79] Some advantages of this approach can be cited, such as low procedural blanks, availability of various types of chromatographic resins, no need to use concentrated reagents (which can cause high levels of blanks and matrix effects), and relative technical simplicity. In addition, the chemical isolation procedure can also act as a preconcentration method, which allows the isotopic analysis to be carried out with higher concentrations of analyte, increasing the precision of data acquisition.[21]

However, a disadvantage associated to ion exchange chromatography is the mass-dependent isotope fractionation, which can occur during analyte interaction between the resin and the mobile phase.[80] Due to the difference in mass between the isotopes of an element, they participate in physical processes or chemical reactions with slightly different efficiency, leading to mass-dependent isotope fraction.[21] This fractionation is also observed in other element isolation procedures in which the analyte is distributed between phases.[81] On-column isotope fractionation is avoided when the analyte interacts only with the mobile phase, not being bound to the resin (stationary phase). In this case, the matrix elements have to be retained on the resin to achieve a suitable isolation. However, in most cases, the analyte shows an interaction with both the ion exchange resin and the mobile phase. Thus, a proper evaluation of the isolation protocol has to be performed, to assure a quantitative recovery of the analyte and to avoid on-column fractionation.[21]

If quantitative recoveries cannot be achieved, the double spike correction approach can be used. In this case, an enriched isotopic spike is added to the sample before isolation. This approach corrects instrumental mass discrimination and on-column mass-dependent isotope fractionation.[21] On the other hand, quantitative recoveries are not necessary when mass-independent variations are being studied or instrumental mass discrimination is corrected using a pair of isotopes of the analyte with small variation in nature (such as can be performed for Sr isotopic analysis).[82]

Another important aspect of chemical isolation for isotopic analysis is regarding the blank levels. Procedural blanks should have the lowest possible concentration, especially when the concentration of the analyte in the sample is at trace levels and/or the isotope ratio variation is small.[82] To achieve low blank values, ultrapure water should be used and inorganic acids should be distilled in a quartz or polytetrafluoroethylene (PTFE) sub-boiling system. The vessels and recipients used for sample decomposition and chemical isolation should be decontaminated before use, in order to minimize their contribution to the blank levels.[42]

In addition, the room air is also a potential source of contamination.[42] This is particularly important when working with elements that are prone to contamination by air, such as Mg. Thus, clean laboratories (or clean rooms) were developed to provide optimum conditions for metal-free sample preparation. Clean laboratories are rooms where the number of airborne particles is controlled, and are designed, constructed, and operated in a manner to control the introduction, generation, and retention of particles inside the room. Clean rooms are classified according to the ISO 14644-1[83] by the maximum number of particles per cubic meter of air. For example, an ISO class 4 clean room (previously classified as class 10 according to the cancelled FED-STD-209E standard) contains less than 83 particles larger than 1 µm per cubic meter.[41,42]

Clean rooms are isolated from the external atmosphere, and the air is filtered through a set of filters with decreasing pore size, refrigerated and dehumidified before introduction into the room. High efficiency particulate air (HEPA) filters are also used. The air is introduced in a laminar top-down flow and in such a way that the pressure inside the room is positive, to prevent particles from entering. In addition, all laboratory components and equipment have to be metal-free to avoid the generation of metal particles. Additionally, users have to wear special suits inside the room and any personal items have to be kept outside the room. Finally, in order to maintain the air of the clean room within specifications, it is necessary to have regular cleanings and change the air filters regularly.[42,83]

The procedures used for Mg chemical isolation from concomitant matrix elements mostly rely on ion exchange chromatography using cationic resins.[84] Commonly used resins include AG 50W-X12 resin and AG 50W-X8 resin.[12,13,85-88]

AG 50W cation exchange resins are composed of sulfonic acid functional groups attached to a styrene divinylbenzene copolymer lattice (Figure 1).[89] The terms X12 and X8 are related to the percentage of crosslinkage of the resin, and determine the bead pore size. A resin with a lower crosslinkage percentage (2 and 4%, X2 and X4) has a more open structure permeable to higher molecular weight substances than a highly crosslinked resin (8, 12 and 16%, X8, X12 and X16). The AG 50W-X12 resin has high separation efficiency, while the AG 50W-X8 allows for a faster separation by gravity.[84,89] In some applications, anionic resins such as AG 1-X8, AG 1-X4 and AG MP-1M were also used.[87,90,91] In several works, the use of a two-stage ion-exchange chromatographic procedure has been reported, in which the sample solution is passed through two columns with different characteristics to assure a complete Mg isolation.[12,85-87] It is important to highlight that an adequate separation of Mg from concomitant matrix elements and quantitative yields are important to obtain accurate isotope ratio results by MC-ICP-MS.[84]

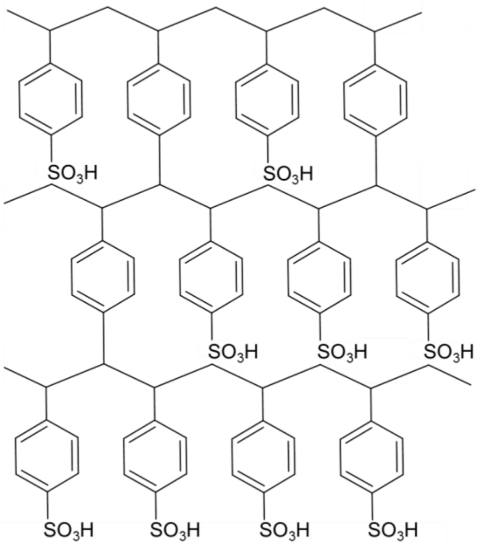

Figure 1. AG 50W cation exchange resin structure representation.

For Sr isolation, the use of an AG50W-X8 cation exchange resin has been reported. In this case, Sr is retained on the resin when 2 mol L^{-1} HCl is used and concomitant elements are eluted from the column. The Sr fraction can later be recovered using 8 mol L^{-1} HCl.[92-94] However, incomplete separation of Sr from other elements (e.g., Ca and Rb) and non-quantitative recoveries have been reported using this resin.[93,95,96] Another possibility is the use of the strontium-specific resin, commercially available as Sr-spec resin (TrisKem International).[10,97,98] This resin contains 4,4′(5′)-di-t-butylcyclohexano-18-crown-6 (Figure 2) in 1-octanol on an inert polymeric support.[99] In a 7 mol L^{-1} HNO_3 medium, Sr is retained on the resin, but can be easily recovered with water or a diluted HNO_3 solution (e.g. 0.5 mol L^{-1} HNO_3).[97]

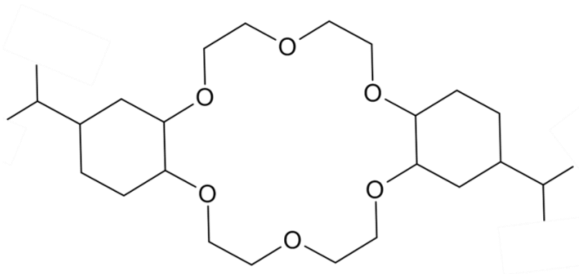

Figure 2. Crown ether 4,4’(5’)-di-tert-butylcyclohexane-18-crown-6 used in the Sr-spec and Pb-spec resins.

In addition, the Sr-spec resin also exhibits an extremely strong Pb retention over a wide range of HNO_3 concentrations, even more strongly than Sr.[100-102] In addition, it is difficult to elute Pb from Sr-spec resin. In order to achieve satisfactory Pb retention and allowing the elution of Pb, a modified version of Sr-spec resin was developed, the Pb spec resin. The Pb-spec resin also contains 4,4′(5′)-di-t-butylcyclohexano-18-crown-6, but in a lower concentration (0.75 mol L^{-1}) than in the Sr-spec resin (1 mol L^{-1}) and is dissolved in an alcohol of higher molecular weight (isodecanol).[99,102] Additionally, Pb isolation can also be performed using an AG1-X8 anion exchange resin with HBr and HCl.[103,104]

Despite the different procedures reported for the purification of Mg, Sr and Pb, there are a few general guidelines for a successful separation: not overloading the column, checking analyte yields for each sample, and checking the concentration of matrix elements in the purified solution. In addition, it is important to fine-tune the column chromatography isolation protocols according to sample solutions obtained upon decomposition methods.[21,105]

2.5 PRINCIPLES OF ICP-MS AND MC-ICP-MS

Inductively coupled plasma-mass spectrometry is the most used technique for elemental determination and isotopic analysis of metals and non-metals in several matrices.[21,43] The main advantages of ICP-MS are the possibility of multi-element determination, low LODs, a wide linear range and high sample throughput. In addition, ICP-MS can easily be coupled to different sample introduction systems (e.g. laser ablation, electrothermal vaporization and cold vapor or hydride generation) and with chromatographic separation techniques (e.g. liquid and gas chromatography). However, despite the advantages presented, this technique is prone to a series of spectral and non-spectral interferences.[43,106]

The ICP-MS instrumentation has three essential parts: (*i*) the ion source, in which the ions are produced, (*ii*) the mass analyzer, in which the ions are separated as a function of their mass-to-charge ratio (m/z), and (*iii*) the detection system, which converts the ion beam into an electrical signal.[21] In addition, the sample introduction system and the interface are also important parts of ICP-MS equipment.[43]

Regarding the mass spectrometers, there are three main types used in commercially available ICP-MS instrumentation: the quadrupole (Q) mass filter, the double-focusing sector field (SF) mass spectrometer and the time of flight (TOF) analyzer.[21] In this work, a sector field ICP-MS (SF-ICP-MS) was used for elemental determination. Additionally, Mg, Sr and Pb isotopic analysis has been carried out using MC-ICP-MS. Thus, the SF mass spectrometer will be described in more detail in this section.

First, some important characteristics of mass spectrometers have to be defined: mass resolution, abundance sensitivity, and scanning speed.[43] Mass resolution provides information on the capability of a mass spectrometer to distinguish between two neighboring ions with a limited difference in mass. One approach used to calculate it is based on the width at 5% of the experimentally observed spectral peak. Another approach considers the valley between two peaks of equal intensity, which are considered separated when the valley intensity does not exceed 10% of the peak heights. Abundance sensitivity is defined as the contribution of the tail of a neighboring peak to the total intensity of the analyte of interest divided by the intensity of the analyte signal. Finally, the scanning speed is defined as the speed in which the mass spectrometer can scan the mass spectrum or can switch from monitoring one m/z to monitoring another.[21,43]

The quadrupole mass filter is the most widespread mass analyzer, mainly due to its technical simplicity and low cost. However, its main disadvantage is the limited mass resolution ($m/\Delta m = 300$), resulting in spectral interferences by polyatomic and isobaric ions.[43,106] The development of collision/reaction cells improved considerably the capability of resolving spectral interferences.[107]

A double-focusing sector field mass spectrometer consists of an electrostatic sector, which selects ions that have the same kinetic energy from an ion beam, and a magnetic sector, which separates the ion beam into discrete ion beams according to their mass-to-charge ratio.[108,109] Sector field mass analyzers can achieve a high mass resolution of up to 10,000. In addition, they also present low abundance sensitivity, high ion transmission efficiency and the ability to generate flat-topped peaks with trapezoidal shape at low mass resolution.[108] The Thermo Scientific Element XR SF-ICP-MS instrument used in this work allows one to work in three different resolution modes: low resolution (LR, R = 300), medium resolution (MR, R = 4000) and high resolution (HR, R = 10,000). However, the sensitivity decreases roughly 10 times when increasing the mass resolution setting from LR to MR or from MR to HR.[110]

For double focusing, both sectors and the way in which they are combined must meet specific requirements.[109] In this sense, three main double-focusing geometries have been developed: Mattauch-Herzog, Nier-Johnson, and reverse Nier-Johnson. The Mattauch-Herzog geometry comprises a 31°50' electrostatic sector followed by a curved 90° magnetic sector, allowing simultaneous monitoring of the entire mass spectrum. In the Nier-Johnson geometry, a 90° electrostatic sector is followed by a 90° magnetic sector. This geometry allows for a simultaneous separation and monitoring of different ion beams and is used in MC-ICP-MS instruments. In the reverse Nier-Johnson geometry, the magnetic sector is located first and is followed by the electrostatic sector. This geometry is preferred for single-collector sector field ICP-MS instruments, since the removal of most of the ions from the beam in the first sector leads to a lower background and a better abundance sensitivity.[21,108,109]

After separation in the mass analyzer, the ion beam is converted into an electrical signal by the detection system. Two types of detectors are commonly used in ICP-MS instruments: the electron multiplier and the Faraday cup.[21] The electron multiplier consists of a continuous dynode electron multiplier or an electron multiplier with discrete dynodes. The ions collide on the surface of the dynode, which releases electrons that are accelerated towards the end of the detector. This acceleration leads to multiple collisions with the inner surface, liberating more electrons, generating an intense pulse for each incoming ion. However, some time is needed before the detector can handle the next ion, called detector dead time, which results in a slightly underestimated count rate for an intense ion beam. Both quadrupole-based and sector field ICP-MS instruments are equipped with an electron multiplier for ion detection.[21,108] The combination of a dual-mode electron multiplier with a Faraday cup detector to increase the linear dynamic range of SF-ICP-MS instruments is also observed.

The Faraday cup is used when relatively intense ion beams have to be measured. It consists of a metallic cup which collects all the ions coming from the mass analyzer. The ions are neutralized by electrons, the resulting current flows via current amplifiers with high-ohmic resistors, and the voltage is measured. The currently used amplifiers show a resistance of 10^{10}, 10^{11}, 10^{12} or 10^{13} Ω. The Faraday cup is very robust and provides a linear and accurate response, but it has lower sensitivity in comparison to the electron multiplier.[21] Multi-collector ICP-MS instruments present an array of Faraday cups as its detection system, which allows simultaneous detection of several ion beams. The position of each detector on the array is adjusted via motorized stages with a precision better than a few micrometers, ensuring the accommodation of several isotopic systems. Faraday cups are preferred over electron multipliers due to their linearity, robustness and accuracy. In addition, they do not suffer from dead time effects.[21] The MC-ICP-MS instrument used in this work is a Thermo Scientific Neptune (Bremen, Germany) installed at the Atomic and Mass Spectrometry unit (A&MS) of the Department of Chemistry at Ghent University. This instrument is equipped with nine Faraday cups connected to 10^{11} or 10^{13} Ω amplifiers (see section 3.1 Instrumentation). A schematic representation of a multi-collector ICP-MS instrument is presented in Figure 3.

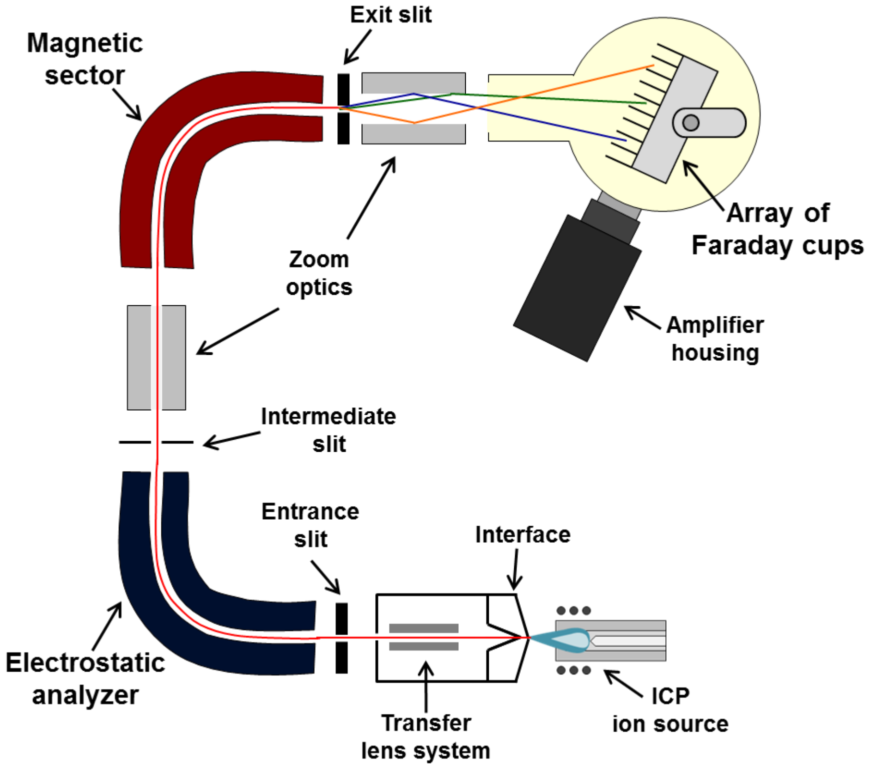

Figure 3. Scheme of a multi-collector ICP-MS instrument (Neptune by Thermo Scientific).[111]

2.5.1 Spectral interferences and matrix effects

An overview of the possible mass spectral interferences on Mg, Sr and Pb isotopes, potentially encountered when determining these elements by means of ICP-MS,[112] is given in Table 3.

Table 3. Potential spectral interferences on Mg, Sr and Pb isotopes by ICP-MS.[112]

	Interference		
Isotope	Isobaric	Polyatomic	Doubly charged
${}^{24}Mg$	-	${}^{12}C^{12}C^{+}$, ${}^{23}Na^{1}H^{+}$ ${}^{6}Li^{18}O^{+}$, ${}^{7}Li^{17}O^{+}$	${}^{47}Ti^{2+}$, ${}^{48}Ti^{2+}$, ${}^{48}Ca^{2+}$, ${}^{49}Ti^{2+}$
${}^{25}Mg$	-	${}^{12}C^{13}C^{+}$, ${}^{12}C^{12}C^{1}H^{+}$, ${}^{9}Be^{16}O^{+}$, ${}^{7}Li^{18}O^{+}$, ${}^{24}Mg^{1}H^{+}$	${}^{49}Ti^{2+}$, ${}^{50}Ti^{2+}$, ${}^{50}Cr^{2+}$, ${}^{50}V^{2+}$, ${}^{51}V^{2+}$
${}^{26}Mg$	-	${}^{12}C^{14}N^{+}$, ${}^{12}C^{12}C^{1}H^{1}H^{+}$, ${}^{12}C^{13}C^{1}H^{+}$, ${}^{10}B^{16}O^{+}$, ${}^{9}Be^{17}O^{+}$, ${}^{25}Mg^{1}H^{+}$, ${}^{24}Mg^{1}H^{1}H$	${}^{51}V^{2+}$, ${}^{52}Cr^{2+}$, ${}^{53}Cr^{2+}$
${}^{84}Sr$	${}^{84}Kr^{+}$	${}^{36}Ar^{48}Ca^{+}$, ${}^{38}Ar^{46}Ca^{+}$, ${}^{40}Ar^{44}Ca^{+}$, ${}^{36}Ar^{48}Ti^{+}$, ${}^{38}Ar^{46}Ti^{+}$, ${}^{66}Zn^{18}O^{+}$, ${}^{67}Zn^{17}O^{+}$, ${}^{68}Zn^{16}O^{+}$	${}^{168}Er^{2+}$, ${}^{168}Yb^{2+}$
${}^{86}Sr$	${}^{86}Kr^{+}$	${}^{38}Ar^{48}Ca^{+}$, ${}^{40}Ar^{46}Ca^{+}$, ${}^{36}Ar^{50}Ti^{+}$, ${}^{38}Ar^{48}Ti^{+}$, ${}^{40}Ar^{46}Ti^{+}$, ${}^{36}Ar^{50}Cr^{+}$, ${}^{68}Zn^{18}O^{+}$, ${}^{70}Zn^{16}O^{+}$, ${}^{69}Ga^{17}O^{+}$, ${}^{70}Ge^{16}O^{+}$	${}^{72}Yb^{2+}$
${}^{87}Sr$	${}^{87}Rb^{+}$	${}^{38}Ar^{49}Ti^{+}$, ${}^{40}Ar^{47}Ti^{+}$, ${}^{36}Ar^{51}V^{+}$, ${}^{70}Zn^{17}O^{+}$, ${}^{69}Ga^{18}O^{+}$, ${}^{71}Ga^{16}O^{+}$, ${}^{70}Ge^{17}O^{+}$	${}^{173}Yb^{2+}$, ${}^{174}Yb^{2+}$, ${}^{174}Hf^{2+}$
${}^{88}Sr$	-	${}^{40}Ar^{48}Ca^{+}$, ${}^{38}Ar^{50}Ti^{+}$, ${}^{40}Ar^{48}Ti^{+}$, ${}^{38}Ar^{50}V^{+}$, ${}^{38}Ar^{50}Cr^{+}$, ${}^{70}Zn^{18}O^{+}$, ${}^{71}Ga^{17}O^{+}$, ${}^{70}Ge^{18}O^{+}$, ${}^{72}Ge^{16}O^{+}$	${}^{176}Yb^{2+}$, ${}^{176}Lu^{2+}$, ${}^{176}Hf^{2+}$
${}^{204}Pb$	${}^{204}Hg^{+}$	${}^{186}W^{18}O^{+}$, ${}^{187}Re^{17}O^{+}$, ${}^{186}Os^{18}O^{+}$, ${}^{187}Os^{17}O^{+}$, ${}^{188}Os^{16}O^{+}$	-
${}^{206}Pb$	-	${}^{188}Os^{18}O^{+}$, ${}^{189}Os^{17}O^{+}$, ${}^{190}Os^{16}O^{+}$, ${}^{190}Pt^{16}O^{+}$	-
${}^{207}Pb$	-	${}^{189}Os^{18}O^{+}$, ${}^{190}Os^{17}O^{+}$, ${}^{191}Ir^{16}O^{+}$, ${}^{190}Pt^{17}O^{+}$	-
${}^{208}Pb$	-	${}^{190}Os^{18}O^{+}$, ${}^{192}Os^{16}O^{+}$, ${}^{191}Ir^{17}O^{+}$, ${}^{190}Pt^{18}O^{+}$, ${}^{192}Pt^{16}O^{+}$	-

The main spectral interferences for Mg isotopes are polyatomic (mainly with carbon) and doubly charged ions.[112] Those interferences can be minimized by chemical isolation of Mg to remove matrix elements prior to determination.[84] However, carbon related interferences can be originated from organic compounds stripped from the resin during the isolation step. Thus, a digestion step should be performed for the Mg fraction collected from the column to avoid those interferences.[13] In addition, the interference from molecular ions such as C_2^+, C_2H^+, $C_2H_2^+$, CN^+ and NaH^+ can be resolved by measuring Mg isotopes at medium or high mass resolution on the left side of the peak, as interferences tend to appear on the right side on the peak,[13,113] as showed in Figure 4.

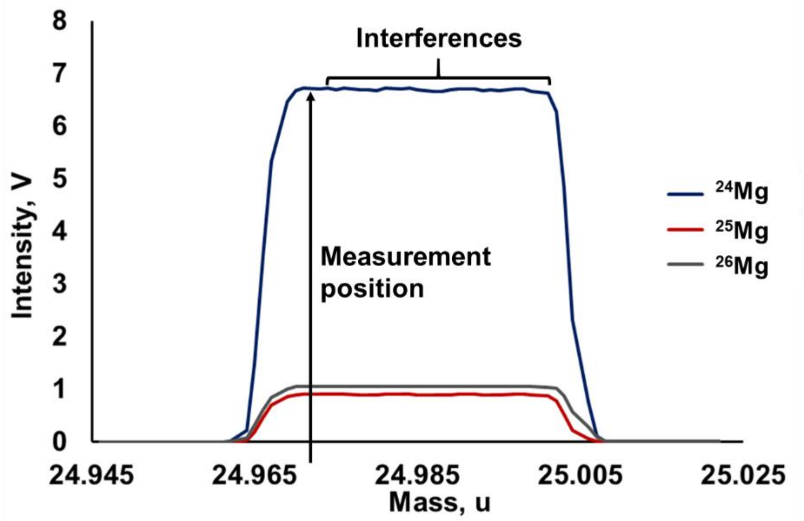

Figure 4. Mass scan during a typical Mg isotopic measurement session by MC-ICP-MS.

In the case of Sr, the most likely interference originates from Rb. Rubidium and strontium are often co-present in samples, since ^{87}Sr is formed by the beta-decay of ^{87}Rb, leading to an isobaric interference on ^{87}Sr.[114] A mass resolution of 300000 is required to resolve this isobaric interference, which is beyond the capabilities of all mass spectrometers.[21] Thus, a chemical isolation procedure is required prior to Sr isotopic analysis in order to separate Rb from Sr. Alternately, the use of a reaction cell (e.g., using CH_3F as reaction gas) enables the determination of the ^{87}Sr/^{86}Sr isotope ratio without chemical isolation.[115] Krypton, which is naturally present in argon gas as an impurity, can also lead to isobaric interferences on ^{84}Sr and ^{86}Sr. Nevertheless, this interference can be easily corrected mathematically by monitoring ^{84}Kr and ^{86}Kr intensities.[97] Interferences from molecular ions such as $ArCa^+$, $ArTi^+$, $ArCr^+$ and ArV^+ can also occur, but the parent elements can be removed by chemical isolation. Potential interferences arising from oxide or doubly charged ions are less likely to occur, because the parent elements have low abundancy or have been already removed in the chemical isolation procedure. In addition, the operating parameters of the ICP mass spectrometer are set to minimize the occurrence of doubly charged ions (< 3%).

For Pb, the interference caused by Hg is the most likely to occur. However, to correct the isobaric overlap of ^{204}Hg on ^{204}Pb, the signal of ^{202}Hg can be monitored and a mathematical correction can be performed.[8] interferences due to oxides of Ir, Os, Pt, Re and W are less likely to occur, because they are not usually in high concentration in samples or they have been already removed in the chemical isolation procedure.

Matrix elements, such as Al, Ca, Fe, K, Mn, Na, Si, and Ti can also cause significant non-spectral interference and affect Mg, Sr and Pb isotopic analysis by MC-ICP-MS.[21] Changes in plasma conditions and repulsion within the ion beam are matrix effects that should be avoided. Additionally, solutions with high carbon content and high acidity can change sample nebulization and analyte ionization.[43] Thus, a suitable matrix removal or analyte isolation protocol is required to obtain accurate results. In addition, matrix and analyte concentration matching between samples and isotopic standards is also a requirement for MC-ICP-MS analysis.

2.5.2 Instrumental mass discrimination

The main drawback of isotopic analysis using ICP-MS is that the data is affected by instrumental mass discrimination (also called mass bias).[21] This phenomenon causes a bias between the measured isotope ratio and the corresponding true value. Isotope ratios obtained by ICP-MS typically deviate from their true values by 1% per mass unit, but this value can reach up to 25% for lighter elements, such as Li.[116]

The causes of instrumental mass discrimination are not entirely understood, but they probably arise during the supersonic expansion of ions passing through the interface and due to space-charge effects. The supersonic expansion occurs in the interface region between the sampler and skimmer cone, as a result of the nozzle effect, which leads to a more efficient extraction of the heavier ions.[117,118] Space-charge effect is a phenomenon that occurs due to the mutual repulsive force between ions of same charge, which cause the lighter ions to be removed from the center of the ion beam.[119,120] Thus, heavier ions are transported more efficiently than lighter ions through the interface, generating a bias in the measured isotope ratio. Matrix elements and target element concentration can also affect instrumental mass discrimination.[121] Thus, isolation of the target element and analyte concentration matching between samples and isotopic standards are performed to minimize this effect. Nevertheless, instrumental mass discrimination needs to be corrected in order to obtain accurate isotope ratio results.

Over the years, several approaches have been proposed to correct instrumental mass discrimination.[21,82] Of these approaches, external standardization with a sample-standard bracketing (SSB) approach has been widely used due to its simplicity.[82] In this case, the correction factor is determined by measuring an isotopic standard of the target element, with known isotopic composition, and comparing the measured isotope ratio to the corresponding true value. In addition, the sample is measured between “brackets”, i.e., the measurement of each sample is preceded and followed by the measurement of the isotopic standard. For the SSB approach to work properly, the mass discrimination of the analyte in samples and standards has to be the same. Therefore, it is of extreme importance to have a perfect separation of matrix elements and to match the analyte concentrations in samples and standards.[21,82] Nevertheless, SSB is often used in combination with other mass discrimination correction approaches.

Another correction approach is internal standardization, which can be performed by using a pair of isotopes of the analyte that is considered to be invariant in nature, or by using a pair of isotopes of another element added to the sample as internal standard.[82] The use of an isotope pair of the analyte has been widely applied for Sr isotope ratios,[10,11,97,98,100] since the $^{88}Sr/^{86}Sr$ ratio is assumed to be constant and can be used for mass discrimination correction of the $^{87}Sr/^{86}Sr$ ratio.[122] This approach can correct for mass discrimination and natural mass-dependent isotope fractionation of the target analyte. In this case, obtaining quantitative recoveries of the analyte in the isolation procedure is not a requirement. However, this approach has limited applicability, almost exclusively for some analytes with radiogenic isotopes.[21,82]

The most common correction approach is the use of a pair of isotopes of another element which is added to the sample as internal standard.[82] To be used as internal standard, the standard should contain at least two isotopes, have a similar mass to the analyte and possess a known isotopic composition (certified isotopic composition).[82] This approach is used for Pb isotope ratios, by using Tl as internal standard.[8,11,123]

Several mass discrimination correction models have been reported, such as linear law, power law and exponential law.[124] However, the exponential Russell’s law[125] still remains the most widely accepted and utilized approach for MC-ICP-MS and can be calculated using the equations 2 and 3:

$$R_{true} = R_{exp} \times \left(\frac{m_i}{m_j}\right)^{\beta} \tag{2}$$

$$\beta = \frac{\ln(R_{true}/R_{exp})}{ln(m_i/m_j)} \tag{3}$$

where R_{exp} is the measured isotope ratio, m_i and m_j are the exact masses of the target element isotopes, R_{true} is the corrected isotope ratio, and β is the mass fractionation coefficient.[125]

The mass fractionation coefficient is calculated for the internal standard and can be applied for mass discrimination correction of the analyte. In this case, it is assumed that the analyte and internal standard have the same behavior.[125] However, instrumental mass discrimination is not constant and can vary in time, due to changes in plasma composition, drifts in mass spectrometer settings and changes of the conditions of the room where the equipment is installed.[21] Thus, further refinements were introduced to account for those changes. Woodhead[126] proposed a model based on a linear relationship between the fractionation coefficients of the analyte and internal standard. Baxter *et al*.[127] have further updated this model and determined a regression line by plotting the natural logarithms of the measured isotope ratios obtained for standard solutions of the analyte and internal standard, of the daily SSB measurements (equation 4):

$$lnR_{analyte,RM} = a + b \times lnR_{IS,RM} \tag{4}$$

where $R_{analyte,RM}$ and $R_{IS,RM}$ are the measured ratios of the analyte and the internal standard for the reference material, respectively. Also, a and b correspond the intercept and slope of the regression line obtained, respectively.

Therefore, the corrected isotope ratio for the sample ($R_{smp,corr}$) can be calculated using equation 5:

$$R_{smp,corr} = R_{smp,obs} \times \frac{R_{analyte,RM}}{e^{a} \times (R_{IS,obs})^{b}} \tag{5}$$

where $R_{smp,obs}$ and $R_{IS,obs}$ are the measured ratios for the analyte and the internal standard in the sample, respectively.[127]

Russell's and Baxter's approaches are currently most often used for instrumental mass discrimination correction in MC-ICP-MS.

3 MATERIALS AND METHODS

In this chapter, the instrumentation, reagents, materials and crude oil samples used in the development of this work will be described. Additionally, the methods and procedures used for Mg, Sr and Pb isotopic analysis of crude oil by MC-ICP-MS will be addressed.

3.1 INSTRUMENTATION

For Mg, Sr and Pb isotope ratio measurements a Thermo Scientific Neptune series MC-ICP-MS instrument (Germany) in operation at Ghent University was used (Figure 5). The multi-collector contains eight movable Faraday cups with *in situ* positional control and one fixed center collector. The Faraday cups can be connected to 10^{11} or 10^{13} Ω amplifiers. The instrument was equipped with an autosampler (ASX-112-FR, Teledyne Cetac Technologies, USA), a perfluoroalkoxy (PFA) concentric nebulizer fitted onto a double spray chamber with cyclonic and Scott-type sub-units, and a quartz torch with an injector (1.0 mm inner diameter). Mg isotope ratio measurements were performed at medium (pseudo) mass resolution on the left side of the peak center, while Sr and Pb isotope ratio were measured at low mass resolution. Instrument settings and data acquisition parameters are summarized in Table 4.

Figure 5. Thermo Scientific Neptune series MC-ICP-MS instrument.

Table 4. Instrument settings and data acquisition parameters for the Thermo Scientific Neptune MC-ICP-MS instrument.

Instrument settings			
Parameter	Mg	Sr	Pb
RF power, W	1200		
Cool gas, L min^{-1}	15		
Auxiliary gas, L min^{-1}	0.6-0.8[a]		
Nebulizer gas, L min^{-1}	0.9-1.1[a]		
Sampling cone	Ni, Jet-type: 1.1 mm orifice diameter		
Skimmer cone	Ni, X-type: 0.8 mm orifice diameter		
Sample uptake, mL min^{-1}	0.1		
Mass resolution mode	Medium[b]	Low	Low
Data acquisition parameters			
Mode	Static, multi-collection		
Integration time, s	4.194		
Number of integrations/ blocks/ cycles	3/10/5	1/6/5	1/7/6
Approach for instrumental mass discrimination correction	SSB	Russell's law using ^{88}Sr/^{86}Sr = 8.375209 + SSB	Baxter's correction using Tl + SSB

Cup configurations							
Mg cup configuration	L3: ^{24}Mg	C: ^{25}Mg	H3: ^{26}Mg				
Amplifier, Ω	10^{11}	10^{11}	10^{11}				
Sr cup configuration	L4: ^{82}Kr	L3: ^{83}Kr	L2: ^{84}Sr	L1: ^{85}Rb	C: ^{86}Sr	H1: ^{87}Sr	H2: ^{88}Sr
Amplifier, Ω	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}
Pb cup configuration	L3: ^{202}Hg	L2: ^{203}Tl	L1: ^{204}Pb	C: ^{205}Tl	H1: ^{206}Pb	H2: ^{207}Pb	H3: ^{208}Pb
Amplifier, Ω	10^{13}	10^{11}	10^{13}	10^{11}	10^{11}	10^{11}	10^{11}

[a] Optimised daily for maximum analyte intensity.

[b] Δm for pseudo-high resolution in MC-ICP-MS is defined as the difference between masses corresponding to 5 and 95 % of the signal intensity at the plateau. A resolving power of 3800 was measured for the medium mass resolution mode. Such a definition exceeds that based on atomic mass difference (10% valley definition) roughly two-fold.[128]

The Mg, Sr and Pb concentration in solutions obtained after sample decomposition and after analyte isolation, as well as other major elements, were determined using a Thermo Scientific Element XR sector field ICP-MS instrument. This instrument was equipped with an autosampler (ASX-520, Teledyne Cetac Technologies, USA) and a 200 µL min^{-1} quartz nebulizer, mounted onto a cyclonic spray chamber. Torch position, gas flow rates and lens settings were optimized daily in order to obtain high signal intensity (Li, In and U) and low oxide levels (UO^+/U^+). Instrument settings and data acquisition parameters are summarized in Table 5.

Table 5. Instrument settings and data acquisition parameters for the Thermo Scientific Element XR SF-ICP-MS instrument.

Parameter	Element XR SF-ICP-MS
RF power, W	1200
Cool gas, L min^{-1}	15
Auxiliary gas, L min^{-1}	0.6-0.9[a]
Nebulizer gas, L min^{-1}	0.9-1.1[a]
Sampling cone	Ni: 1.1 mm orifice diameter
Skimmer cone	Ni, H-type: 0.8 mm orifice diameter
Scan type	EScan
Mass window, %	100
Search window, %	80
Integration window, %	60
Samples per peak	25
Monitored nuclides	
Low mass resolution mode	^{7}Li, ^{9}Be, ^{59}Co, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{95}Mo, ^{115}In[b], ^{138}Ba, ^{208}Pb
Medium mass resolution mode	^{23}Na, ^{24}Mg, ^{27}Al, ^{44}Ca, ^{48}Ti, ^{55}Mn, ^{56}Fe, ^{60}Ni, ^{115}In[b]
High mass resolution mode	^{39}K, ^{115}In[b]

[a] Optimised daily for maximum analyte intensity and low oxide levels

[b] Used as internal standard

Samples were digested by MAWD-PDC using a high-pressure Multiwave 7000 microwave unit (Anton Paar, Austria). This unit is equipped with a rack with capacity for five 80 mL pressure-sealed quartz vials and a stainless-steel microwave digestion cavity with a polytetrafluoroethylene liner (1 L). The maximum temperature, pressure and microwave power that the system can attain is 300 °C, 199 bar and 1700 W, respectively.

An analytical balance (model AY 220, resolution of 0.1 mg, Shimadzu, Japan) was used for sample weighing. Nylon membranes were dried in an oven at 105 °C (Nova Ética, Brazil). An automatic titrator (model 836, Metrohm, Switzerland) equipped with a magnetic stirrer (module 803 Ti Stand), 20 mL buret (Dosino 800), and a platinum electrode (model 8.109.1306, Metrohm) was used for water content determination in crude oil. The determination of API gravity was performed using a viscosimeter (model SVM 3000, Anton Paar, Austria).

All statistical calculations, including Student's *t*-test (confidence level of 95%) and, in some cases, one-way analysis of variance (ANOVA), were performed using GraphPad InStat (GraphPad InStat Software Inc, Version 3.00, 1997) software. All isolation and evaporation procedures were carried out in a metal-free class-10 clean lab facility at Ghent University (Picotrace, Germany).

3.2 REAGENTS AND MATERIALS

All reagents used throughout the experiments were of high-purity grade. Water (18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Merck Millipore, USA). Trace metal analysis grade nitric acid (68%, 1.42 kg L^{-1}, Fisher Chemicals, United Kingdom) and hydrochloric acid (37%, 1.18 kg L^{-1}, Fisher Chemicals) were purified in a sub-boiling unit (Savillex DST-4000, Savillex Corporation, USA). Ultrapure hydrogen peroxide (9.8 mol L^{-1}) and ACS grade acetone were purchased from Sigma Aldrich (Belgium). Trace metal grade hydrofluoric acid (47−51%) was acquired from Seastar Chemicals Inc. (Canada). Toluene (Sigma-Aldrich, Germany) was used in the solubilization method. For water content determination, the Karl Fischer (two-component) reagent, Composite 5® (Sigma-Aldrich, Germany), was used and samples were solubilized using a mixture of toluene (Tedia, Brazil) and methanol (Carlo Erba Reagents, Italy) (3:1).

For Mg isolation, 2 mL polypropylene columns (Eichrom Technologies, France) and AG50WX8 strong cation exchange resin (hydrogen form, 100–200 mesh size, Bio-Rad, USA) were used. One mL polypropylene BioSpin columns (Bio-Rad) and Sr resin (SR-B100-A, 100-150 µm, TrisKem International, France) were used for Sr and Pb isolation.

For the determination of Mg, Sr and Pb, as well as other major elements, by SF-ICP-MS a multi-element standard solution (10 mg L^{-1}) prepared by dilution of 1000 mg L^{-1} stock solutions (Merck, Germany) in 2% (v/v) HNO_3 was used. Calibration curves were prepared by sequential dilution of the multi-element standard in the range of 0.1 to 30 µg L^{-1} in 2% (v/v) HNO_3. An In solution (1000 mg L^{-1}, Merck) was added as an internal standard (final concentration of 1 µg L^{-1}) to correct instrument instability and matrix effects.

For Mg isotope ratio measurements, the ERM-AE143 reference material acquired from BAM (Federal Institute for Materials Research and Testing, Germany)[129] and the widely accepted DSM3[130] Mg were used. A standard Mg solution (Inorganic Ventures, USA, lot K2-MG650434) was used as an in-house isotopic standard. For Sr isotopic analysis, NIST SRM 987 isotopic reference material obtained from the National Institute for Standards and Technology (NIST, USA) was used. For Pb, isotopic reference materials of Pb (NIST SRM 981) and Tl (NIST SRM 997) were used. Two standard solutions of Pb (Inorganic Ventures, lot G2-PB03044 and lot D2-PB03020) were used as in-house isotopic standards. These solutions were characterized in other works[8,123] and will be termed as “Pb in-house I” and “Pb in-house II”. All in-house isotopic standard solutions were used daily for validation of the accuracy and precision of the isotope ratio measurements and did not go through sample preparation.

High purity argon (99.998%, Air Liquide, Belgium) was used for plasma generation and nebulization in the SF-ICP-MS and MC-ICP-MS equipment.

3.3 DECONTAMINATION OF MATERIALS

The materials used in the development of this work, such as glassware, pipet tips, acid containers and auto-sampler vials were decontaminated by immersion in 50% (v/v) HCl for at least 24 h on a hot plate (110 °C). After, it was washed and immersed in ultrapure water for another 24 h on a hot plate. Finally, the material was washed with ultrapure water and dried.

Savillex® PFA beakers were washed with soap and water to remove any sample residue and then decontaminated on a hot plate (110 °C) using the following protocol: 50% HNO_3 for 24 h; washed with ultrapure water; 50% HNO_3 for 24 h; washed with ultrapure water; HCl 50% for 24h; washed with ultrapure water; HCl 50% for 24 h; washed with ultrapure water; dried on a hot plate. This protocol was carried out in a metal-free class-10 clean lab facility.

The quartz vessels used for MAWD-PDC were decontaminated with 6 mL of HNO_3 14.4 mol L^{-1} using the following irradiation program: 10 min ramp to 200 °C, temperature kept for 10 min. At the end of the program, the acidic residue was discarded; the vessels were washed with ultrapure water and dried with compressed air.

3.4 SAMPLES

Five crude oil samples named “A” to “E” from different reservoirs in Brazil, with API gravity ranging from 26 to 28 (medium crude oil), were used in the development of this work. As there are no crude oil reference materials with certified isotopic compositions for Sr, Mg or Pb, a standard reference material, SRM 1634c (trace elements in fuel oil) from the National Institute of Standards and Technology (NIST) was used in this context. Before the analysis, samples were manually homogenized for 5 min.

3.4.1 Crude oil characterization

3.4.1.1 API gravity

The determination of API gravity was performed according to ASTM D5002.[131] For this, approximately 5 mL of crude oil was introduced into a viscosimeter set at 40 °C with the aid of a syringe. The API gravity value was calculated from the density values.

3.4.1.2 Water content

The water content determination in crude oil samples was performed according to ASTM D4377[132] using the Karl Fischer method. A sample mass of up to 1 g was introduced into the coulometric cell with the aid of a syringe and solubilized in a mixture of toluene and methanol (3:1). After, the mixture was titrated using the Karl Fischer reagent, Composite 5®.

3.4.1.3 Sediment content

Sediment content determination was performed according to ASTM D4807[33]. For this, sample masses ranging from 1 to 10 g were weighed into a glass beaker and 100 mL of toluene were added. This mixture was heated up to 90 °C and filtered under vacuum through a 0.45 µm porosity nylon membrane filter (Sigma-Aldrich, Germany). The membrane filter was washed with hot toluene (at 90 °C), dried in an oven (105 °C), and weighed for sediment content determination.

3.4.1.4 Elemental characterization

Crude oil samples were digested by MAWD-PDC (as will be described in section 3.5.1) for further determination of major and minor elements by SF-ICP-MS.

3.5 CRUDE OIL DECOMPOSITION METHODS

3.5.1 Microwave-assisted wet digestion with a pressurized digestion cavity (MAWD-PDC)

For MAWD-PDC, 500 mg of crude oil were weighed inside quartz vessels, 6 mL of 14.4 mol L^{-1} HNO_3 were added, and vessels were placed in the microwave rack. Samples were pre-digested for 1 h at 100 °C, by immersing the rack with the vessels in a boiling water bath. After, the rack was placed inside the liner already filled with 150 mL of water and 5 mL of 14.4 mol L^{-1} HNO_3. The microwave cavity was pressurized at 40 bar N_2 for digestion. The microwave heating program was: (i) 5 min ramp to 90 °C; (ii) 10 min ramp to 110 °C, temperature kept for 5 min; (iii) 10 min ramp to 120 °C; (iv) 10 min ramp to 130 °C; and (v) 20 min ramp to 250 °C, temperature kept for 15 min. After cooling, the digests were collected in Savillex® PFA beakers and evaporated to near dryness at 90 °C.

3.5.2 Solubilization of inorganic solids after ASTM D4807

For the method of solubilization of inorganic solids after ASTM D4807,[33] 2 to 10 g of crude oil were weighed in a glass beaker and solubilized in 100 mL of toluene. This mixture was heated at 90 °C and filtered under vacuum through a 0.45 µm nylon membrane filter. After, the membrane was washed with hot toluene (at 90 °C) and dried in an oven at 105 °C for 20 min. The dried membrane was then transferred into a polypropylene vessel containing 25 mL of water and stirred for 1 h in a mechanical stirring system (TE 420, Tecnal, Brazil). Elements present as inorganic solids in crude oil, such as Mg and Sr, are extracted and subsequently dissolved under these conditions. Finally, the solutions were transferred to Savillex® PFA beakers and evaporated to near dryness at 90 °C.

3.6 ISOLATION PROTOCOLS

The isolation protocols evaluated in this work for Mg, Sr, and Pb are summarized in Table 6.

Table 6. Summary of isolation protocols evaluated for Mg, Sr, and Pb isolation.

	Analyte			
Step	Mg	Sr	Sr and Pb	Pb
Resin	1 mL of AG50W-X8	300 µL of Sr-spec	300 µL of Sr-spec	300 µL of Pb-spec
Cleaning	10 mL H_2O 30 mL 7 mol L^{-1} HCl 20 mL H_2O	1 mL H_2O 1 mL 6 mol L^{-1} HCl 1 mL H_2O	6 mL H_2O 10 mL 6 mol L^{-1} HCl 3 mL H_2O	10 mL H_2O 6 mL of 0.05 mol L^{-1} $(NH_4)_2C_2O_4$
Conditioning	10 mL 0.4 mol L^{-1} HCl	1 mL 7 mol L^{-1} HNO_3	1 mL 7 mol L^{-1} HNO_3	2 mL 1 mol L^{-1} HNO_3
Sample loading	1 mL in 0.4 mol L^{-1} HCl	1 mL 7 mol L^{-1} HNO_3	1 mL in 7 mol L^{-1} HNO_3	1.5 mL 1 mol L^{-1} HNO_3
Matrix removal	28 mL 0.4 mol L^{-1} HCl 3 mL 0.15 mol L^{-1} HF* 10 mL 0.5 mol L^{-1} HCl: 95% acetone* 1 mL 0.8 mol L^{-1} HCl	5 mL 7 mol L^{-1} HNO_3	4 mL 7 mol L^{-1} HNO_3	10 mL 0.1 mol L^{-1} HNO_3
Analyte elution	23 mL 0.8 mol L^{-1} HCl	5 mL 0.05 mol L^{-1} HNO_3	4 mL H_2O (Sr collection) 1 mL 3 mol L^{-1} HCl (change of medium) 4 mL 8 mol L^{-1} HCl (Pb collection)	10 mL 0.05 mol L^{-1} $(NH_4)_2C_2O_4$.

*evaluated for digests and extracts.

For Mg isolation, 1 mL of the AG50W-X8 strong cation exchange resin was loaded into a 2 mL polypropylene column with an inner diameter of 0.8 cm (Figure 6, A and B).[12,13] The isolation procedure of Mg was optimized and adapted to the composition of crude oil digests/extracts. Thus, the necessity to use 0.15 mol L^{-1} HF and a mixture of 0.5 mol L^{-1} HCl: 95% acetone for matrix elution was evaluated. For Sr isolation, a procedure using 300 µL of Sr-spec resin in 1 mL polypropylene columns was evaluated. In addition, a procedure for sequential Sr and Pb isolation was evaluated; using 1 mL polypropylene columns loaded with 300 µL of Sr-spec resin were used (Figure 6, C and D).[11,97] Moreover, a procedure using the 300 µL of Pb-spec resin was evaluated for Pb isolation only.

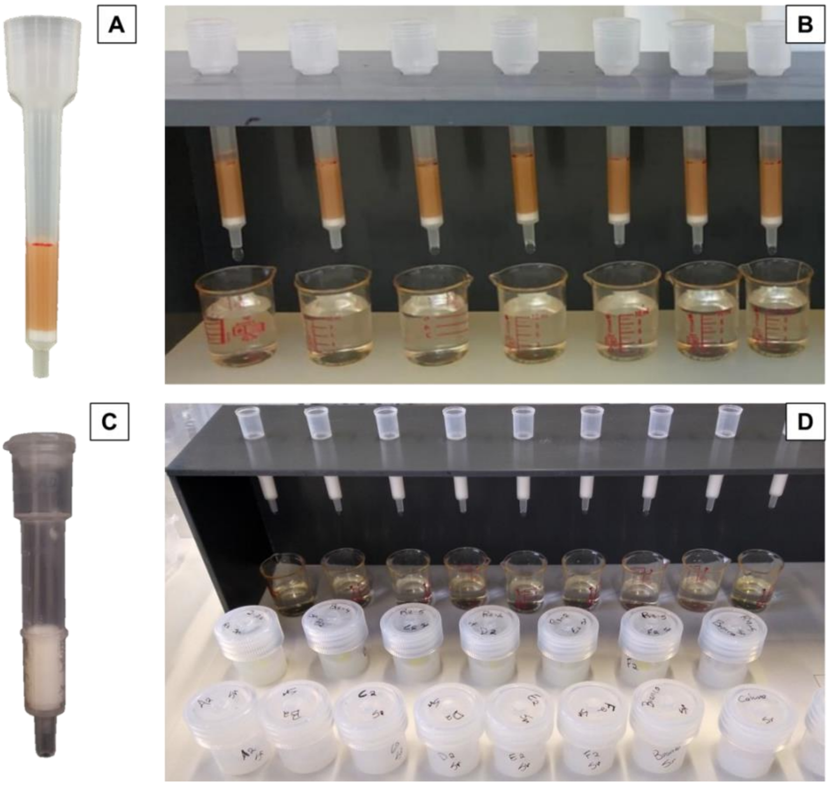

Figure 6. A) polypropylene column loaded with 2 mL of AG50W-X8 resin; B) setup for Mg isolation; C) polypropylene column loaded with 300 µL of Sr-spec resin; D) setup for Sr and Pb isolation.

After analyte elution, the fractions collected in Savillex® PFA beakers were evaporated to near dryness at 90 °C and re-dissolved in 2 mL of 14.4 mol L^{-1} HNO_3, after which the beakers were closed and heated on a hot plate at 110 °C overnight. This digestion step was carried out for the removal of organic compounds (predominantly acetone, in addition to resin material). After that, the pure fractions were evaporated to near dryness at 90 °C and the residues were subsequently re-dissolved in 1 mL of 2% (v/v) HNO_3 for element determination and isotope ratio measurements. Two procedural blanks were included in each batch of samples (10 columns). All the steps of solubilization, evaporation to near dryness, target element isolation and related procedures were carried out in a metal-free class-10 clean lab facility.

3.7 Mg, Sr AND Pb ISOTOPE RATIO MEASUREMENTS

For Mg, Sr and Pb isotope ratio measurements, each crude oil sample was analyzed in triplicate, including sample preparation and analyte isolation, with each purified target element fraction being measured three times.

Magnesium isotope ratio measurements were carried out following a protocol described earlier.[13,129] External correction for instrumental mass discrimination was accomplished using ERM-AE143 as an external standard, measured in a sample-standard bracketing (SSB) approach. Samples and standards were diluted in 2% (v/v) HNO_3 to approximately 60 µg L^{-1} of Mg (for solutions obtained after MAWD-PDC) or 150 µg L^{-1} of Mg (for solutions obtained after solubilization). The Mg in-house standard and DSM3 solution were measured regularly for quality control purposes.[13,129] The $^{26}Mg/^{24}Mg$ and $^{25}Mg/^{24}Mg$ ratios were expressed in delta notation ($\delta^{26}Mg$ and $\delta^{25}Mg$, in per mil, ‰) relative to DSM3, and calculated according to the following equation:

$$\delta^{x/24}Mg = \left[\frac{\left(\frac{^{x}Mg}{^{24}Mg}\right)_{smp}}{\left(\frac{^{x}Mg}{^{24}Mg}\right)_{DSM3}} - 1\right] \times 1000 \qquad (6)$$

where x is 25 or 26.

Strontium isotope ratio measurements were performed following a protocol described earlier by De Muynck *et al.*[97] All samples were measured in a SSB sequence with a solution of the isotopic reference material NIST SRM 987 as bracketing isotopic standard. The purified fractions and standards were diluted in 2% (v/v) HNO_3 to 60 and 150 µg L^{-1} of Sr for the analysis of solutions obtained upon MAWD-PDC and solubilization, respectively. Although Sr was isolated from the matrix components and from Rb by means of the Sr-spec resin, the signal of ^{85}Rb was measured to perform a mathematical correction for the remaining Rb. The contribution of Rb at *m/z* 87 was corrected by using the Rb isotopic composition as provided in the IUPAC table[133] for mathematical correction. The contribution of ^{86}Kr on ^{86}Sr was corrected by monitoring ^{82}Kr using the Kr isotopic composition as provided in the IUPAC table.[133] Instrumental mass discrimination was corrected using Russell's equation:[125,134]

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{smp,corr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_{smp,obs} \times \left(\frac{m_{87}}{m_{86}}\right)^{\beta} \qquad (7)$$

where $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{smp,obs}}$ is the measured ratio, m_{86} and m_{87} are the exact masses for ^{86}Sr and ^{87}Sr isotopes, respectively and $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{smp,corr}}$ is the corrected ratio. The mass fractionation coefficient β is obtained by:

$$\beta = \frac{ln\left[\frac{\left(\frac{^{88}Sr}{^{86}Sr}\right)_{cert}}{\left(\frac{^{88}Sr}{^{86}Sr}\right)_{obs}}\right]}{ln\left(\frac{m_{88}}{m_{86}}\right)} \qquad (8)$$

where $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{cert}}$ = 8.375209 (the value conventionally accepted by the International Union of Geosciences),[135] $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{obs}}$ is the measured ratio, m_{86} and m_{88} are the exact masses for ^{86}Sr and ^{88}Sr isotopes, respectively.

An additional SSB external correction using NIST SRM 987 was applied to correct for potential minor drift using equations showed below:

$$\delta^{87}Sr_{smp} = \left[\frac{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{smp,corr}}{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{NIST987}} - 1\right] \times 1000 \qquad (9)$$

where $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{NIST987}}$ is the NIST SRM 987 ratio average before and after the analysis of the sample.

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{smp} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_{NIST987,cert} \times \left[\frac{\delta^{87}Sr_{smp}}{1000} + 1\right] \qquad (10)$$

where $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{NIST987,cert}}$ = 0.710248 ± 0.000012 (the certified NIST SRM 987 ratio).[97]

Lead isotope ratio measurements were performed following a protocol described earlier.[8,123] Samples and NIST SRM 981 Pb solution were diluted with 2% (v/v) HNO_3 to 15 µg L^{-1} of Pb. NIST SRM 997 Tl was added to samples and standards at a concentration of 5 µg L^{-1}. The measurement of ^{202}Hg and ^{204}Pb was performed using the Faraday cups L3 and L1 connected to 10^{13} Ω resistors. To correct for the contribution of the isobaric overlap of ^{204}Hg on ^{204}Pb, the ^{202}Hg signal was monitored and the Hg isotopic composition as provided in the IUPAC table[133] was relied on for mathematical correction. Correction for instrumental mass discrimination was accomplished following the method described by Baxter *et al.*[127] relying on spiked Tl as an internal standard. With this method, a regression line in ln–ln space is determined by measuring both the isotope ratio for Tl in NIST SRM 997 (^{205}Tl/^{203}Tl) and that selected for Pb in NIST SRM 981 in a series of standard solutions. Based on the regression line obtained and the Tl isotope ratio measured for NIST SRM 997 Tl, the mass bias is corrected, according to the equation below:

$$\left(\frac{^{x}Pb}{^{y}Pb}\right)_{smp,corr} = \left(\frac{^{x}Pb}{^{y}Pb}\right)_{smp,obs} \times \frac{\left(\frac{^{x}Pb}{^{y}Pb}\right)_{NIST981,cert}}{e^{a} \times \left[\left(\frac{^{205}Tl}{^{203}Tl}\right)_{NIST997,obs}\right]^{b}} \qquad (11)$$

where $(^{x}\mathrm{Pb}/^{y}\mathrm{Pb})_{\mathrm{smp,obs}}$ is the measured ratio, $(^{x}\mathrm{Pb}/^{y}\mathrm{Pb})_{\mathrm{NIST981,cert}}$ is the certified NIST SRM 981 ratio, $(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_{\mathrm{NIST977,obs}}$ is the ratio observed for NIST SRM 997. Also, a and b correspond the intercept and slope of the regression line obtained.

This method was followed by an external correction via a SSB approach:

$$\delta^{x}Pb_{smp} = \left[\frac{\left(\frac{^{x}Pb}{^{y}Pb}\right)_{smp,corr}}{\left(\frac{^{x}Pb}{^{y}Pb}\right)_{NIST981}} - 1\right] \times 1000 \qquad (12)$$

where $(^{x}\mathrm{Pb}/^{y}\mathrm{Pb})_{\mathrm{NIST981}}$ is the NIST SRM 981 ratio average before and after the analysis of the sample.

$$\left(\frac{^{x}Pb}{^{y}Pb}\right)_{smp} = \left(\frac{^{x}Pb}{^{y}Pb}\right)_{NIST981,cert} \times \left[\frac{\delta^{y}Pb_{smp}}{1000} + 1\right] \qquad (13)$$

where $(^{x}\mathrm{Pb}/^{y}\mathrm{Pb})_{\mathrm{NIST981,cert}}$ is the certified NIST SRM 981 ratio.

Figure 7 shows a flowchart summarizing all experiments and methods performed in this work.

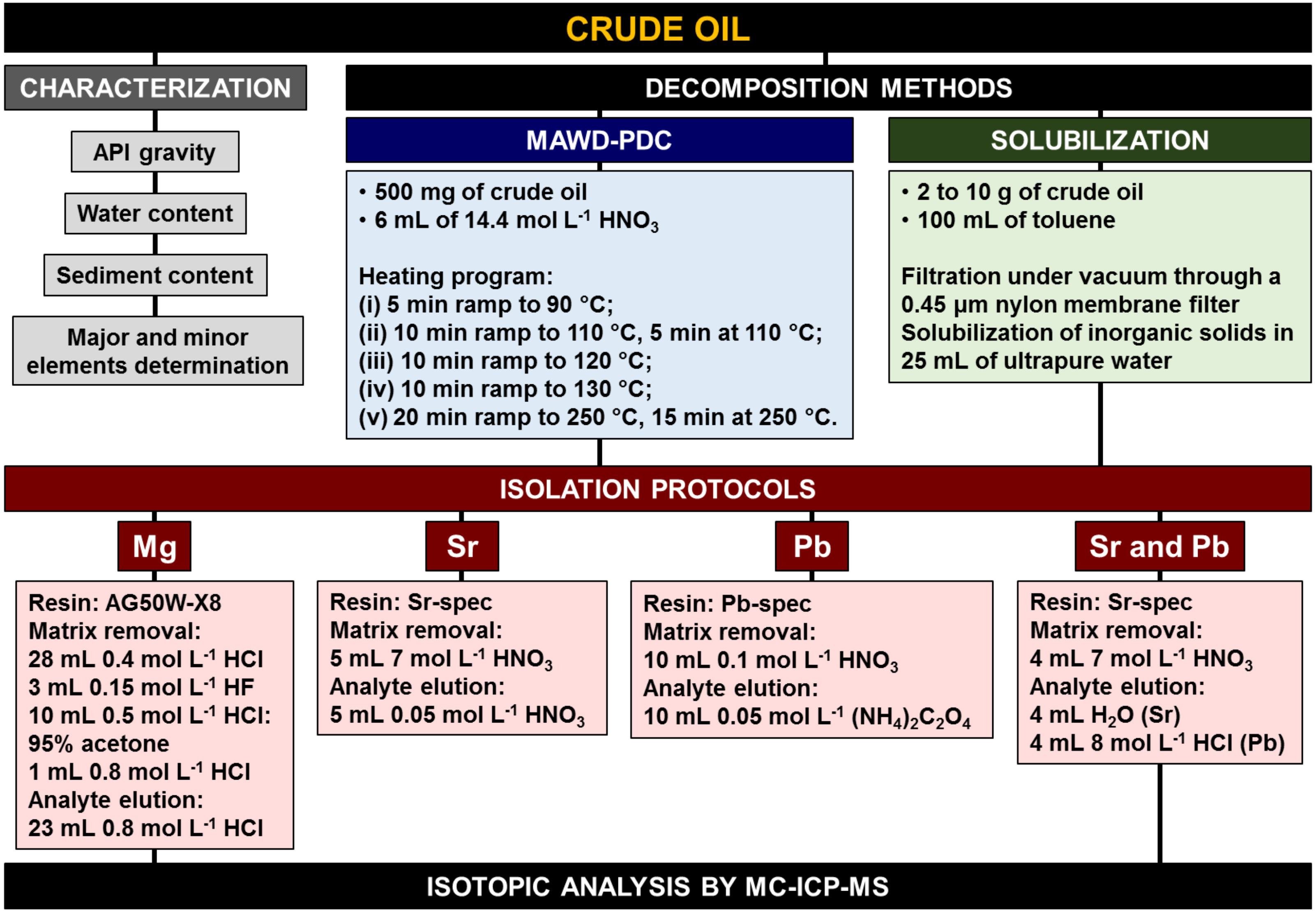

Figure 7. Flowchart of experiments and methods performed in this work.

4 RESULTS AND DISCUSSION

In this chapter the results obtained during the development of methods for the determination of isotope ratios of Mg, Sr and Pb in crude oil by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) will be presented and discussed. Two sample preparation methods, (i) microwave-assisted wet digestion within an ultra-high pressure digestion cavity (MAWD-PDC) and (ii) solubilization of inorganic solids as obtained after the ASTM D4807 test method, were evaluated for crude oil decomposition. Column chromatographic protocols for analyte isolation were evaluated and fine-tuned for Mg, Sr, and Pb, to ensure quantitative recoveries. After establishing the optimum conditions for crude oil decomposition and analyte isolation, the methods developed in this work were applied for Mg, Sr and Pb isotope ratios determination by MC-ICP-MS.

4.1 CRUDE OIL CARACTERIZATION

Crude oil samples used in this work were characterized for API gravity, water and sediment content and results are presented in Table 7. API gravity of crude oils ranged from 26.3 (sample C) to 28.2 (sample A), which are considered as medium crude oils. In relation to the water content, sample D showed the highest water content (5.55%), while sample C presented only 0.36% of water. The determination of sediment content was performed according to ASTM D4807.[33] It should be mentioned that for samples B, D and E the mass used for filtration was lower than recommended by the ASTM (10 g), once the sediment content of those samples was higher than 0.15%.[33] When 10 g of sample were used, obstruction of the nylon membrane pores occurred and filtration was stopped. The sediment content ranged from 0.05% in crude oil C to 0.86% in crude oil D. In addition, it is possible to observe a relation between the sediment and water content. Crude oils with higher water content also present higher sediment content.

Table 7. Results of API gravity, water, and sediment content in samples of medium crude oil.

Sample	API gravity	Water, %	Sediment, %
A	28.2 ± 0.1	0.82 ± 0.04	0.131 ± 0.045
B	27.3 ± 0.3	1.97 ± 0.03	0.377 ± 0.012
C	26.3 ± 0.1	0.36 ± 0.03	0.054 ± 0.009
D	26.8 ± 0,2	5.55 ± 0.03	0.864 ± 0.147
E	26.4 ± 0.1	0.93 ± 0.01	0.299 ± 0.010

In addition, crude oil samples were digested by MAWD-PDC for the determination of major and minor elements by SF-ICP-MS. For this, 500 mg of crude oil were digested using 6 mL of 14.4 mol L^{-1} HNO_3. Results are shown in Table 8.

Table 8. Elemental composition of crude oils obtained via SF-ICP-MS after MAWD-PDC (mean ± standard deviation, n = 3).

	Concentration, $\mu g\ g^{-1}$				
Element	A	B	C	D	E
Al	12.8 ± 0.6	7.19 ± 0.20	26.9 ± 2.1	9.96 ± 0.70	6.31 ± 0.20
Ba	8.81 ± 0.46	2.08 ± 0.18	0.232 ± 0.05	6.90 ± 0.35	11.3 ± 0.2
Be	< 0.0002[a]	< 0.0002[a]	< 0.0002[a]	< 0.0002[a]	< 0.0002[a]
Ca	251 ± 35	236 ± 10	3.57 ± 0.10	512 ± 36	208 ± 12
Co	0.018 ± 0.001	0.015 ± 0.002	0.133 ± 0.04	0.035 ± 0.005	0.131 ± 0.009
Fe	1.33 ± 0.06	3.62 ± 0.25	3.91 ± 0.07	29.8 ± 1.8	3.68 ± 0.15
K	6.09 ± 0.97	15.7 ± 0.7	2.02 ± 0.20	56.7 ± 4.0	1.98 ± 0.24
Li	0.023 ± 0.001	2.15 ± 0.06	0.044 ± 0.042	0.432 ± 0.045	0.095 ± 0.005
Mg	12.5 ± 1.9	50.7 ± 3.6	3.27 ± 0.33	199 ± 10	33.7 ± 1.5
Mn	0.045 ± 0.008	0.159 ± 0.005	0.013 ± 0.001	3.09 ± 0.22	0.250 ± 0.010
Mo	0.058 ± 0.005	0.074 ± 0.003	0.040 ± 0.002	0.139 ± 0.05	0.070 ± 0.005
Na	49.9 ± 7.6	955 ± 40	161 ± 10	2930 ± 268	257 ± 16
Ni	6.61 ± 1.0	6.75 ± 1.50	4.70 ± 0.7	5.70 ± 0.60	12.2 ± 0.9
Pb	0.203 ± 0.024	0.059 ± 0.006	0.091 ± 0.007	0.193 ± 0.017	0.161 ± 0.012
Rb	0.017 ± 0.002	0.055 ± 0.009	0.019 ± 0.002	0.144 ± 0.010	0.013 ± 0.001
Sr	2.86 ± 0.13	5.95 ± 0.34	0.340 ± 0.050	20.3 ± 1.0	12.8 ± 0.8
Ti	< 0.05[a]	< 0.05[a]	< 0.05[a]	< 0.05[a]	< 0.05[a]
V	8.93 ± 0.44	8.73 ± 0.55	1.90 ± 0.14	14.1 ± 0.9	15.9 ± 1.1
Zn	1.44 ± 0.10	1.44 ± 0.05	0.353 ± 0.045	1.20 ± 0.10	0.263 ± 0.007

[a] LOQ (10 SD) obtained by SF-ICP-MS

It is possible to observe that the concentration of metals in crude oil samples varied in a wide range. However, a higher concentration of alkaline and alkaline-earth elements was observed in all crude oils, such as Ca and Na, since these elements are mostly present in crude oil.[3] Moreover, the concentration of other alkaline and alkaline-earth elements, such as Ba, Be, K, Li, Mg, Rb, and Sr, was much lower than the values obtained for Ca or Na. It can be observed that the content of alkaline and alkaline-earth elements seems to be correlated with the water and sediment content of crude oils. For example, sample D, which has the highest value of water and sediment, also presented the higher concentration of alkaline and alkaline-earth elements. Information about the concentration of those elements in crude oil is of extreme importance, since they can cause several problems during crude oil refining, such as fouling and corrosion of equipment. In addition, elements such as Co, Mn, Mo, Pb and Ti were present in concentrations lower than 0.5 µg g^{-1} in most crude oils.

4.2 CRUDE OIL DECOMPOSITION METHODS

When considering crude oil digestion, converting the samples into aqueous solutions compatible with determination techniques is not a simple task due to the high chemical resistance of this matrix.[22,32,55,73] The methods typically used for the preparation and analysis of crude oil have some limitations, such as the use of a low sample mass, low throughput and/or high limits of quantification (LOQs).[22] In this work, two sample preparation methods were compared for crude oil decomposition and subsequent Mg, Sr and Pb isotopic analysis. Crude oil samples were decomposed by MAWD-PDC and solubilization of inorganic solids after ASTM D4807.[33]

For MAWD-PDC, 500 mg of crude oil were digested with 6 mL of 14.4 mol L^{-1} HNO_3 using a 75 min digestion program as described in section 3.5.1. The digestion program presented a very long heating ramp (60 min up to 250 °C). However, a sudden pressure increase occurred at about 120 °C; leading to the projection of the crude oil and the microwave program had to be stopped. This probably occurred due to the presence of a high content of volatile organic compounds in the crude oil, which react violently with nitric acid.[3,22] Thus, to avoid crude oil projection during digestion, samples were pre-digested at 100 °C by immersing the vessels in a boiling water bath for 1 h. This step promoted the oxidation of the lighter crude oil fractions. Afterwards, samples were subjected to the same program described in section 3.5.1. Figure 8 shows the temperature and pressure profile of crude oil digestion by MAWD-PDC after the pre-digestion step.

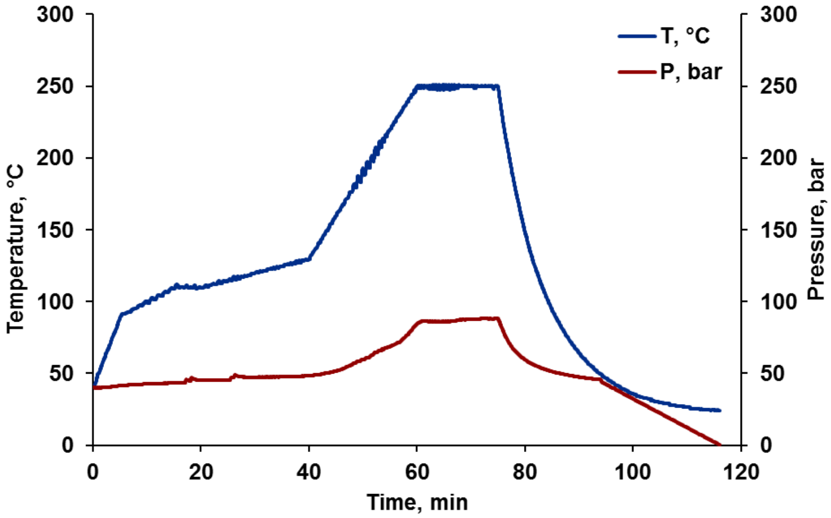

Figure 8. Temperature and pressure profile during digestion of crude oil by MAWD-PDC.

As can be observed in Figure 8, no sudden increase of pressure as occurred during crude oil digestion. In addition, the maximum temperature and pressure achieved during digestion were 250 °C and 88.6 bar, respectively. As the PDC system allows the use of up to 199 bar,[25] these conditions were considered adequate for crude oil digestion. After digestion of crude oil by MAWD-PDC, clear pale-yellow solutions were obtained and carbon content was lower than 2000 mg L^{-1}. Considering the dilution factor used for sample analysis (at least 100 fold), no carbon interference was observed.

For the method of solubilization of inorganic solids after ASTM D4807[33] crude oil was solubilized in toluene and filtered through a 0.45 µm nylon membrane filter. The membrane filter retained crude oil inorganic solids, which contain elements such as Mg and Sr. After drying, the membrane was transferred to a polypropylene vessel containing 25 mL of water and stirred to recover Mg and Sr. Clear colourless solutions were obtained using this method.

The Mg and Sr concentrations obtained using both sample preparation methods are shown in Table 9. In addition, Pb concentrations obtained after MAWD-PDC are shown. It is important to highlight that the solubilization after ASTM D4807 method was not suitable for Pb recovery, because Pb is not retained on the nylon membrane filter. Possibly, this analyte is present in crude oil as organic complexes that are not retained with the inorganic fraction present in crude oil.[3]

Table 9. Results for Mg, Sr and Pb concentrations obtained by SF-ICP-MS after MAWD-PDC and solubilization after ASTM D4807 (mean of 3 independent digestions ± standard deviation).

Sample	Method	Concentration, µg g^{-1}		
		Mg	Sr	Pb
A	MAWD-PDC	12.5 ± 1.9	2.86 ± 0.13	0.203 ± 0.024
	Solubilization	9.98 ± 1.54	2.30 ± 0.40	nd
B	MAWD-PDC	50.7 ± 3.6	5.95 ± 0.34	0.059 ± 0.006
	Solubilization	48.6 ± 1.9	6.06 ± 0.21	nd
C	MAWD-PDC	3.27 ± 0.33	0.340 ± 0.050	0.091 ± 0.007
	Solubilization	2.93 ± 0.13	0.324 ± 0.016	nd
D	MAWD-PDC	199 ± 10	20.3 ± 1.0	0.193 ± 0.017
	Solubilization	201 ± 9	19.5 ± 1.1	nd
E	MAWD-PDC	33.7 ± 1.5	12.8 ± 0.8	0.161 ± 0.012
	Solubilization	32.5 ± 1.5	12.8 ± 0.7	nd

nd: not determined

As observed in Table 9, the results obtained for Mg and Sr after MAWD-PDC were in good agreement with those obtained after solubilization and no statistical difference was observed (*t*-test, 95% of confidence level). In addition, a reference material of residual fuel (NIST 1634c) was digested by MAWD-PDC. The results obtained for Mg, Sr and Pb (1.67 ± 0.12, 0.386 ± 0.022, 0.412 ± 0.020 µg g^{-1}, respectively) were in agreement with the data reported in previous works (1.69 ± 0.07 and 1.78 ± 0.23 µg g^{-1} for Mg, 0.390 ± 0.020 µg g^{-1} for Sr and 0.380 ± 0.014 µg g^{-1} for Pb).[136,137] Thus, it can be inferred that both crude oil pretreatment methods provided quantitative recoveries for Mg and Sr, enabling their application for isotopic analysis. In addition, although the solubilization method was not suitable for Pb recovery, the MAWD-PDC method provided accurate results for this element. The concentrations of Mg and Sr in the crude oils analyzed in this work range from 2.93 to 201 µg g^{-1} and 0.32 to 20 µg g^{-1}, respectively. As expected, the concentration of Pb in crude oil samples was very low, ranging from 0.059 to 0.203 µg g^{-1}.

When comparing the two sample preparation methods used in this work, the method of solubilization allows to process a higher sample mass (from 2 g for sample D to up to 10 g for sample A and C) compared to the MAWD-PDC method (500 mg). This is an important aspect when considering the determination of elements present in low concentration in crude oil (e.g., Pb and in some cases Sr). In addition, it is also important when considering the isotopic analysis of Mg, Sr and Pb by MC-ICP-MS, in which roughly 1 mL of sample diluted to 150 µg L^{-1} is needed. Moreover, limits of quantification (LOQs) obtained by SF-ICP-MS after MAWD were 0.7, 0.1 and 0.02 ng g^{-1} for Mg, Sr and Pb, respectively (500 mg of crude oil, 1 mL of final volume). After solubilization, LOQs obtained by SF-ICP-MS were 0.2 and 0.02 ng g^{-1} for Mg and Sr, respectively (2000 mg of sample, 1 mL of final volume).

A comparison of sample preparation methods used for Sr and Pb isotopic analysis of crude oil reported in the literature is provided in Table 10. In addition, the methods used in this work are also shown. It can be highlighted that only few publications reported the isotopic analysis of Pb[16-19] in crude oil and only one work was found for Sr.[20] In addition, no publications have reported on Mg isotopic analysis of crude oil. Thus, it can be inferred that information about the isotopic composition of Mg, Sr and Pb in crude oil is still lacking, requiring the development of methods for this purpose. It can be observed in Table 10 that previous publications rely on the use of conventional sample preparation methods, such as acid digestion followed by dry ashing,[20] liquid-liquid extraction[16,17] or high-pressure asher digestion.[18,19] The use of ultra-high pressure systems with microwave radiation (as MAWD-PDC) was not yet reported for isotopic analysis of crude oil. Those systems allow for the fast heating of the sample and for digestion temperatures and pressures higher (up to 300 °C and 199 bar) than those of conventional systems (280 °C and 80 bar). Thus, bringing important advantages over the previous reported approaches. In addition, the method of solubilization of inorganic solids after the ASTM D4807 was not yet reported for elemental or isotopic analysis of crude oil. This method does not require any sophisticated equipment, using only equipment usually available in analytical chemistry laboratories (e.g., simple glass labware, vacuum pump and filter membranes). Moreover, with the solubilization method it is possible to use a high sample mass (up to 10 g) and the use of halogenated solvents is not required.

Table 10. Summary of sample preparation methods reported in the literature for Sr and Pb isotopic analysis of crude oil.

Analyte	Sample preparation and analyte isolation procedure	Technique	Ref.
Sr	3.5 g of crude oil were digested with a mixture of HNO_3 and H_2O_2 at 120 to 160 °C. Then, samples were ashed in a muffle furnace at 300 to 350°C for 8 h. Residues were dissolved in 2 mol L^{-1} HNO_3 and Sr isolation was performed using Sr-Spec resin. After matrix elution with 7 mol L^{-1} HNO_3, the Sr fraction was eluted using 0.05 mol L^{-1} HNO_3.	TIMS	20
Pb	5 ml of crude oil were dissolved in dichloromethane and mixed with 1.5 mol L^{-1} HBr. After mixing, the aqueous phase (HBr) was separated and collected. After collection, HBr was added again to the organic phase and the extraction repeated. Aqueous phases were evaporated to dryness overnight (110 °C) and residues were digested using a mixture of HNO_3 and H_2O_2. Finally, 6 mol L^{-1} HCl was added and the samples were evaporated to dryness. Residues were dissolved in 2 mol L^{-1} HBr and Pb isolation was performed using AG1-X8 resin. After matrix elution with 2 mol L^{-1} HBr, the Pb fraction was eluted using 6 mol L^{-1} HCl.	MC-ICP-MS	16,17
Pb	0.5 g of crude oil was digested in a high-pressure asher with a mixture of HNO_3 and H_2O_2 at 320 °C for 90 min. For some samples it was necessary to digest 4 aliquots of 0.5 g due to the low Pb concentration. The four digests were combined and evaporated to dryness. The residue was dissolved in 2% HNO_3. For derivatization, samples were mixed with a buffer solution and the pH was adjusted to 4.9. Then, isooctane and 1% $NaBEt_4$ were added and the mixture was manually shaken for 5 min. The isooctane supernatant was collected for analysis.	GC-MC-ICP-MS	18
Pb	Sample preparation was performed as described for reference 18. After evaporation of the digests, the residues were dissolved in 0.5 mol L^{-1} HBr and centrifuged for 20 min at 4000 rpm. Pb isolation was performed using AG1-X8 resin. After matrix elution with 0.5 mol L^{-1} HBr and 0.2 mol L^{-1} HCl, the Pb fraction was eluted using 6 mol L^{-1} HCl.	MC-ICP-MS	19
Mg, Sr and Pb	*i*) 0.5 g of crude oil was digested by MAWD-PDC using 14.4 mol L^{-1} HNO_3 at 250 °C for 75 min. *ii*) 2 to 10 g of crude oil were solubilized in toluene (at 90 °C) and filtered through a nylon membrane filter. The membrane was washed with hot toluene (at 90 °C), dried in an oven (105 °C) and transferred into a vessel containing ultrapure water for analyte dissolution. After evaporation at 90°C (for both, MAWD-PDC and ASTM procedures) the residues were dissolved as follows: in 0.4 mol L^{-1} HCl for Mg isolation or in 7 mol L^{-1} HNO_3 for Sr and Pb isolation. Mg isolation was performed using AG50WX8 strong cation exchange resin. After matrix elution with 0.4 mol L^{-1} HCl and 0.5 mol L^{-1} HCl: 95% acetone (only for digests), the Mg fraction was eluted using 0.8 mol L^{-1} HCl. Sr and Pb isolation were performed using a Sr-spec resin. After matrix elution with 7 mol L^{-1} HNO_3, the Sr and Pb fractions were eluted with H_2O and 8 mol L^{-1} HCl, respectively.	MC-ICP-MS	This work

4.3 ISOLATION PROTOCOLS

For an accurate and precise determination of the isotopic composition of a target element in a sample, it is important to avoid, or at least accurately correct for, spectral and non-spectral interferences, which are factors that might compromise the attainable accuracy and precision. The best way to manage such interferences is to separate the target element from it concomitant matrix in a quantitative way. Using this approach, the analyte is, ideally, obtained free from interfering species, and the matrix of the sample can be carefully matched to that of the standard solutions. In this work, extraction chromatographic separations were evaluated and fine-tuned for Mg, Sr and Pb isolation from crude oil matrix.

4.3.1 Mg isolation

The procedures used for Mg chemical isolation from concomitant matrix elements reported in the literature mostly rely on ion exchange chromatography using cationic resins.[84] Commonly used resins include AG 50W-X12 resin and AG 50W-X8 resin.[12,13,85-88] In some applications, anionic resins such as AG 1-X8, AG 1-X4 and AG MP-1M were also used.[87,90,91] The cation exchange resin AG 50W-X8 was already described in previous papers to isolate Mg from geological[12] and biological materials.[13] Thus, it will be used in this work.

It is important to mention, that not only the isolation protocol, but also the determination of Mg isotopes by MC-ICP-MS are both sensitive to the elemental composition of sample solutions.[21,84] Thus, in order to avoid spectral and non-spectral interferences, the Mg isolation procedure needed to be fine-tuned to the composition of crude oil solutions obtained upon MAWD-PDC and solubilization. In addition, the elemental composition of the solutions obtained after MAWD-PDC and solubilization are significantly different, as showed in Table 11 for crude oil D. After MAWD-PDC, all matrix elements are present in the final solution, while some elements are not recovered via the solubilization method. The signal intensities by SF-ICP-MS of Al, Be, Co, Fe, Mo, Ni, Pb, Ti, and Zn in solutions obtained after the solubilization method never exceeded the levels of background noise. Additionally, it is possible to observe that the concentrations of Mn, Rb and V after solubilization were significantly lower than those obtained after MAWD-PDC. In this sense, two different isolation protocols were optimized, one for MAWD-PDC and another for solubilization as a sample preparation method.

Table 11. Elemental composition obtained via SF-ICP-MS of crude oil D after MAWD-PDC or solubilization (mean ± standard deviation, n = 3).

	Concentration, µg g^{-1}	
Element	MAWD-PDC	Solubilization
Al	9.96 ± 0.70	-
Ba	6.90 ± 0.35	6.60 ± 0.26
Be	< 0.0002[a]	-
Ca	512 ± 36	506 ± 20
Co	0.035 ± 0.005	-
Fe	29.8 ± 1.8	-
K	56.7 ± 4.0	50.9 ± 3.7
Li	0.432 ± 0.045	0.384 ± 0.017
Mg	199 ± 10	201 ± 9
Mn	3.09 ± 0.22	0.060 ± 0.009
Mo	0.139 ± 0.05	-
Na	2930 ± 268	2824 ± 130
Ni	5.70 ± 0.60	-
Pb	0.193 ± 0.017	-
Rb	0.144 ± 0.010	0.117 ± 0.007
Sr	20.3 ± 1.0	19.5 ± 1.1
Ti	< 0.05[a]	-
V	14.1 ± 0.9	0.063 ± 0.010
Zn	1.20 ± 0.10	-

[a] LOQ (10 SD) obtained by SF-ICP-MS

For Mg isolation, 1 mL of AG50W-X8 strong cation exchange resin was loaded into a 2 mL polypropylene column. The resin was first cleaned with 10 mL H_2O, 30 mL 7 mol L^{-1} HCl, and 20 mL H_2O, to avoid any contamination from the resin. After conditioning of the resin with 10 mL of 0.4 mol L^{-1} HCl, 1 mL of the sample solution (in 0.4 mol L^{-1} HCl) was loaded onto the column. The Mg elution profiles for crude oil D after MAWD-PDC are presented in Figure 9 (A and B). It is possible to see that matrix elements such as K and Na were already eluted with 0.4 mol L^{-1} HCl. Afterwards, the necessity of using a solution of hydrofluoric acid in the isolation protocol was investigated. Thus, the isolation procedure for digests was carried out with (Figure 9-A) and without the use of 0.15 mol L^{-1} HF (Figure 9-B). Previous works reported the use of HF mainly to elute Al, Be and Ti.[12,13] In the case of crude oils evaluated in this work, it was possible to observe that the concentration of Be and Ti was below the limit of quantification (as can be seen in Table 8, crude oil characterization). Additionally, it can be observed from Figure 9 that the use of HF was not necessary for Al elution, as the Al elution peak was well separated from that of Mg even without this reagent. This comes as an advantage, since HF is a highly corrosive reagent and is potentially toxic. Hence, it was possible to elute Al using 7 mol L^{-1} HCl after Mg collection. Moreover, the use a solution of 0.5 mol L^{-1} HCl:95% acetone was suitable for the elution of Fe, Mn and Zn prior Mg collection, as also demonstrated in previous works.[12,13]

It is possible to see in Figure 9 (A and B) that Ca and K partially co-elute with Mg in the collected fraction (shaded section). However, the concentration of K measured in the purified Mg fraction was negligible for all crude oil samples. Furthermore, for samples B, C, and D, and the Ca/Mg elemental ratio in the purified Mg fraction was below 0.3. Grigoryan *et al*.[14] previously demonstrated that Ca/Mg ratios lower than 1.5 do not affect the results of Mg isotope ratio measurements. Only when the Ca/Mg ratios are higher than 1.5 an overall shift of the δ^{26}Mg value towards a lighter Mg isotopic composition can be observed.[14] For the samples A and E, the Ca/Mg ratio in the purified Mg fraction was 5 and 2, respectively. These samples showed a high initial Ca/Mg ratio (20 and 6 for sample A and E, respectively). In this case, in order to reduce the Ca/Mg ratio and avoid biased Mg isotope ratio results, the Mg isolation was repeated prior analysis by MC-ICP-MS. After the second isolation step, the Ca/Mg ratio in the purified fraction was below 1.5. Additionally, quantitative Mg recoveries should be obtained after the isolation procedure, in order to avoid biased results. Thus, the Mg concentration in purified fractions was measured by SF-ICP-MS and recoveries obtained after isolation of crude oil digests ranged between 96 and 106%, with an average recovery of 99 ± 7%.

As already demonstrated, elements such as Al, Be, Co, Fe, Mo, Ni, Pb, Ti, and Zn are not recovered using the solubilization method, possible because those elements are not present as inorganic salts or are not retained in the membrane filter in the process of crude oil filtration. Thus, the Mg isolation protocol evaluated for solutions obtained by this method was carried out without using a solution of HF. Moreover, the necessity of using the mixture of 0.5 mol L^{-1} HCl:95% acetone was evaluated (Figure 9, C and D). This solution is used mainly to elute Fe and Mn, but

Fe was not recovered and the concentration of Mn in solutions obtained upon solubilization was significantly lower than those obtained upon MAWD-PDC (Table 11). The signal intensity of Mn in the 0.5 mol L^{-1} HCl:95% acetone fraction did not exceed the levels of background noise and the concentration of Mn measured in the purified Mg fraction was negligible for all crude oil samples. Therefore, the use of acetone is not required for Mg isolation, which reduces the time needed for isolation and the consumption of reagents. Additionally, it also allowed avoiding organic solvents in the purified sample.

A partial co-elution of Ca with Mg was also observed. However, the Ca/Mg ratio in the purified Mg fraction was below 0.3 for samples B, C, and D. Samples A and E were subjected to the isolation procedure twice, in order to reduce the Ca/Mg ratio. Quantitative Mg recoveries were obtained (from 95 to 104%, with an average recovery of 99 ± 3%) following this isolation protocol for solutions obtained after the solubilization method.

After Mg collection, an additional matrix elution step was performed, using 7 mol L^{-1} HCl, in order to elute elements such as Al, Ca and Sr, which were still retained on the resin. Subsequently, the resin was regenerated, in order to be used again. This procedure consisted of rinsing the resin with 10 mL H_2O, 30 mL 7 mol L^{-1} HCl, and 20 mL H_2O, the same procedure used to pre-clean the resin before use. No negative effects on the matrix removal efficiency, as well as on Mg recoveries were observed using the regenerated resin. Thus, the AG50W-X8 was used at least twice before being discarded.

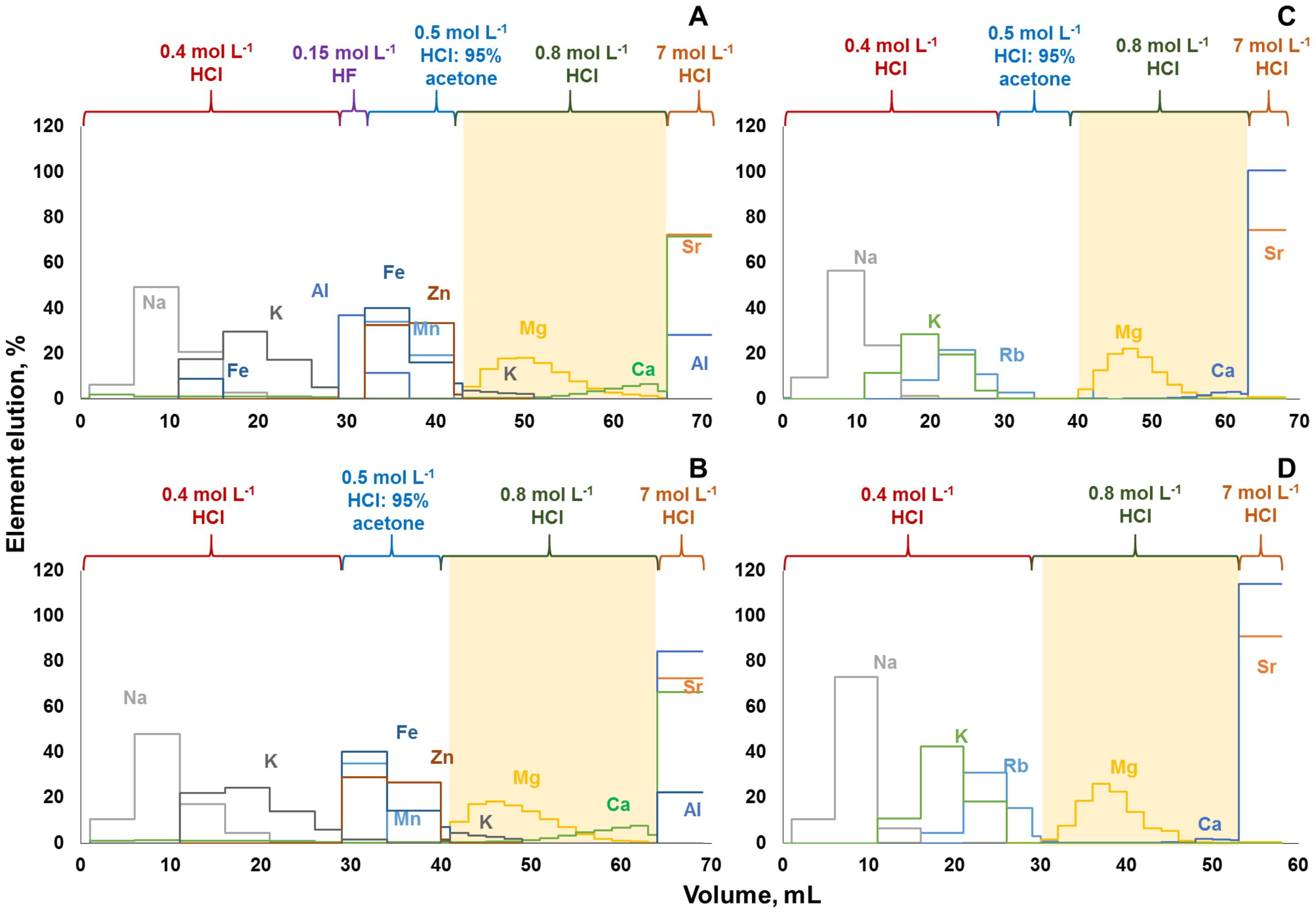

Figure 9. Elution profile for crude oil D by SF-ICP-MS after MAWD-PDC, (A) using 0.15 mol L^{-1} HF and (B) without using HF, and after solubilization, (C) using acetone and (D) without acetone. The shaded sections represent the collected fractions.

4.3.2 Sr and Pb isolation

A possibility for Sr isolation is the use of the Sr-spec resin, which contains 1 mol L^{-1} 4,4′(5′)-di-t-butylcyclohexano-18-crown-6 (crown ether) in 1-octanol on an inert polymeric support. The specific combination of crown ether concentration and alcohol constitutes the resin selective to Sr.[96,99] The Sr-spec resin has been used to isolate Sr from a variety of samples, such as environmental samples, geological and archeological materials.[10,97,98]

Initially, the procedure previously described by De Muynck *et al*.[97] was used for Sr isolation from solutions obtained after solubilization of crude oil. In this procedure, 300 µL of the Sr-spec resin is loaded into the column and cleaned with 1 mL of H_2O, 1 mL 6 mol L^{-1} HCl and 1 mL of H_2O. Afterwards, the resin is conditioned with 1 mL of 7 mol L^{-1} HNO_3, followed by loading 1 mL of the sample solution in 7 mol L^{-1} HNO_3 onto the resin. Matrix elements are eluted using 5 mL of 7 mol L^{-1} HNO_3. At 7 mol L^{-1} HNO_3 Sr displays a high affinity with the resin, being retained into the column.[97] This behavior can be explained by the capacity factor k’, which can be defined as the ratio between the number of moles of the analyte in the stationary phase (resin) and the mobile phase (HNO_3 solution).[138] Thus, the higher the capacity factor, the higher is the affinity of the analyte with the resin. Horwitz *et al*.[99] determined the capacity factor k’ of Sr and other elements (Ba, Ca, Cs, K, Na, Pb, and Rb) using the Sr-spec resin as a function of the HNO_3 concentration. The k’ for Sr at 7 mol L^{-1} is about 90, while other elements such as Ba, Ca, Cs, K, Na, and Rb display a k’ value not higher than 3. On the other hand, at this concentration, Pb displays an affinity that is even higher than that of Sr (k’ of about 700).[99]

Additionally, Horwitz *et al*.[99] also observed that at lower HNO_3 concentrations (e.g. 0.05 mol L^{-1}) the capacity factor of Sr decreased (about 0.7). Under these conditions, also the capacity factor of Pb decreases (about 300), but remains sufficiently high to retain Pb on the column. Thus, Sr was further eluted from the column using 5 mL of 0.05 mol L^{-1} HNO_3. Using this procedure, Sr recoveries ranged between 75 and 104%, with an average recovery of 88 ± 9%. Moreover, the concentration of matrix elements (e.g. Ba, Ca, K, Na, and Rb) in the purified Sr fraction was negligible.

Although the procedure using the Sr-spec resin was considered suitable for Sr isolation from crude oil matrix, a sequential isolation protocol for Sr and Pb, previously described by Smet *et al*.,[11] was evaluated. As already mentioned, the Sr-spec resin exhibits an extremely strong Pb retention over a wide range of HNO_3 concentrations. Consequently, after Sr elution with diluted HNO_3, Pb remains into the column. However, Pb can be eluted from the column using a solution of HCl.

Thus, for Sr and Pb isolation, 300 µL of Sr-spec resin was loaded into column and cleaned with 10 mL 6 mol L^{-1} HCl and 3 mL H_2O, to avoid any contamination from the resin. After conditioning of the resin with 1 mL of 7 mol L^{-1} HNO_3, 1 mL of the sample solution (in 7 mol L^{-1} HNO_3) was loaded onto the column. Figure 10 shows the elution profiles of Sr and Pb for a synthetic standard solution containing the major elements present in crude oil digests, in addition to 1000 µg L^{-1} of Sr and 100 µg L^{-1} of Pb.

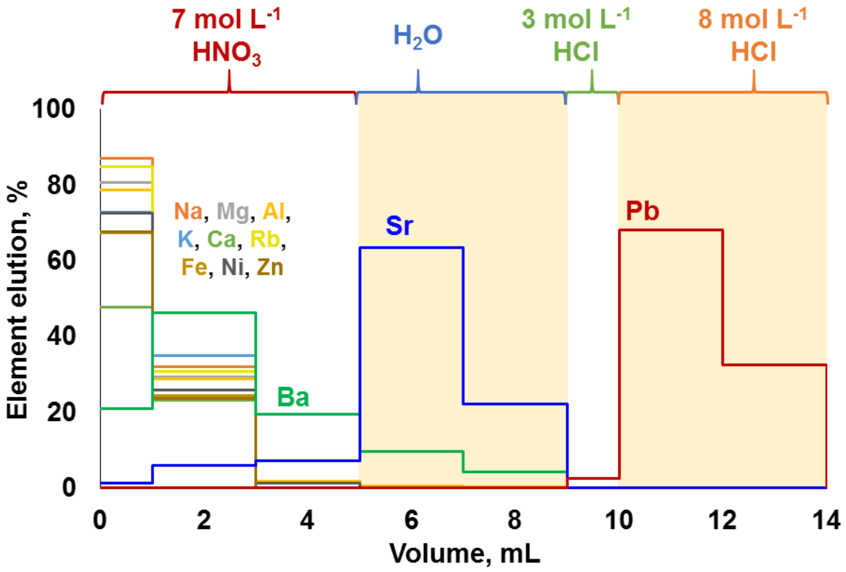

Figure 10. Elution profiles of Sr and Pb using Sr-spec resin. The shaded sections represent the collected fractions.

The chromatographic procedure applied to crude oil proved to efficiently separate Sr from Rb, and to completely remove concomitant major elements, including Al, Ca, Fe, K, Mg and Na. Aluminum, Ca, K, Mg, Na, and Rb were eluted during the first step of the isolation procedure, using 7 mol L^{-1} HNO_3, and co-elution of Rb with Sr was not observed for any crude oil sample. Afterwards, Sr was eluted using ultrapure water only. Although Ba partially co-eluted with Sr (Ba/Sr ratio of 0.16) during the elution experiment, no Ba was observed in the Sr fraction of real crude oils. The Sr recoveries for the crude oil samples ranged between 71 and

105%, with an average recovery of 90 ± 10% for the digests obtained after MAWD-PDC, and 82 ± 8% for the solutions obtained after solubilization.

After the elution of Sr, it was possible to elute Pb using a solution of 8 mol L^{-1} HCl. Similarly to what was observed by Smet *et al*.,[11] a small fraction (about 2.5%) of the Pb present already eluted from the column in the step using 1 mL of 3 mol L^{-1} (used for change of medium), which could cause Pb isotopic fractionation. However, Smet *et al*.[11] previously reported that the isolation process using Sr-spec resin did not induce on-column isotopic fractionation for Pb. The average recovery for Pb from the crude oil digests was 97 ± 2%. Moreover, the concentration of concomitant matrix elements in Sr and Pb purified fractions was negligible. Thus, this procedure was considered suitable for sequential Sr and Pb isolation from crude oil matrix.

After Sr and Pb isolation, the resin was regenerated, in order to be used again. This procedure consisted of rinsing the resin with 10 mL 6 mol L^{-1} HCl and 3 mL H_2O, the same procedure used to pre-clean the resin before use. Matrix removal efficiency and Sr and Pb recoveries using the regenerated resin were similar to those obtained using a new resin. Thus, the Sr-spec resin was used twice before being discarded.

Another possibility for Pb isolation is the use of a modified version of the Sr-spec resin, the Pb-spec resin.[102] The Pb spec resin contains the same crown ether as the Sr-spec resin, but in a lower concentration (0.75 mol L^{-1}) and dissolved in isodecanol. The Pb-spec resin was evaluated for Pb isolation from crude oil digests following the procedure described by De Muynck *et al*.[139] For this, 300 µL of Pb-spec resin was loaded into column and cleaned with 10 mL H_2O and 6 mL of 0.05 mol L^{-1} $(NH_4)_2C_2O_4$. After conditioning of the resin with 2 mL of 1 mol L^{-1} HNO_3, 1.5 mL of analyte solution (in 1 mol L^{-1} HNO_3) was loaded onto the column. Figure 11 shows the elution profile Pb for a synthetic standard solution containing the major elements present in crude oil digests and 100 µg L^{-1} of Pb.

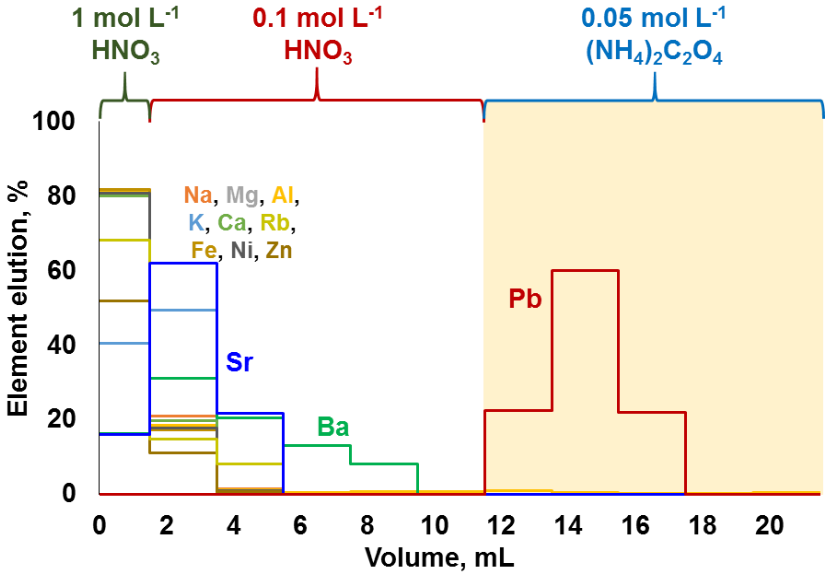

Figure 11. Elution profile of Pb using Pb-spec resin. The shaded section represents the collected fraction.

As can be observed, elements such as Al, Ba, Ca, Fe, K, Mg, Na, Ni, Rb, Sr, and Zn are eluted from the column using 1 and 0.1 mol L^{-1} HNO_3. Horwitz *et al*.[102] determined the capacity factor k’ of Pb and other elements (Ba, Ca, K, Na, Sr, and Tl) on Pb-spec resin as a function of the HNO_3 concentration. They observed that Pb capacity factor at 1 mol L^{-1} HNO_3 is about 1000, so that Pb is retained onto the resin. In addition, at 0.1 mol L^{-1} HNO_3 the capacity factor of elements such as Ba, Ca, K, Na, and Sr is lower than 2, causing those elements to be eluted from the column, while Pb capacity factor remains sufficiently high (about 500) being retained onto the resin.[102] No data are available on the capacity factors of Al, Fe, Mg, Ni, and Zn, which eluted from the column using 0.1 mol L^{-1} HNO_3. Pb was eluted from the column using a solution of 0.05 mol L^{-1} $(NH_4)_2C_2O_4$. The recovery for Pb from the synthetic standard solution was about 104% and the concentration of matrix elements in the purified fraction was negligible. Thus, this procedure can also be used for Pb isolation from crude oil matrix.

It was possible to observe that both resins, Sr-spec and Pb-spec, were characterized by quantitative yields and matrix elements removal, and could be used for Sr and Pb isolation. However, the sequential isolation protocol using the Sr-spec resin was used for Sr and Pb isolation from solutions obtained after solubilization and MAWD-PDC, in order to increase sample throughput, minimize reagents consumption and residues generation.

4.4 Mg, Sr AND Pb ISOTOPE RATIOS OF CRUDE OIL

After establishing the optimum conditions for crude oil decomposition and analyte isolation, the methods developed in this work were applied for Mg, Sr and Pb isotope ratios determination by MC-ICP-MS. For Mg, as the ERM-AE143[140,141] Mg reference material is more readily available compared to the widely accepted DSM3 standard, the samples and standards were measured relative to ERM-AE143. However, the results were recalculated and expressed relative to the DSM3 isotopic reference material using delta notation (in per mil, ‰).[129] Each crude oil sample was analyzed in triplicate, including sample preparation and Mg isolation, and measured three times. Results for the Mg isotopic composition of crude oil samples are presented in Table 12.

The Mg isotope ratios obtained by MAWD-PDC and solubilization were in good agreement and no statistical difference was observed (*t*-test, 95% of confidence level). Thus, both sample preparation methods can be used for Mg isotopic analysis of crude oil. When Mg isotope ratios, δ^{26}Mg and δ^{25}Mg, of crude oil were plot against each other, it was possible to observe that results lie in a single line. This line is known as the mass-dependent Mg isotope fractionation line and indicates that no mass-independent isotope effect or polyatomic interference has occurred during analysis.[13] The δ^{26}Mg in crude oil ranged between -1.53 and -0.71‰, which is within the range between seawater ($\delta^{26}Mg_{DSM3}$ = -0.83 ± 0.11‰)[142] and marine carbonates of biogenic origin ($\delta^{26}Mg_{DSM3}$ = -5.57 to -1.04‰).[143] Additionally, an aliquot of NIST 1634c residual fuel was digested by MAWD-PDC and its Mg isotopic composition was determined to be δ^{26}Mg = -0.86 ± 0.04‰ and δ^{25}Mg = -0.44 ± 0.02‰. It can be highlighted that, as to date, no Mg isotope ratios of crude oil have been reported yet.

For Sr isotope ratio measurements, all samples were measured in a SSB sequence with a solution of the isotopic reference material NIST SRM 987 as bracketing isotopic standard and the instrumental mass discrimination was corrected using Russell's equation.[97,125] ^{87}Sr/^{86}Sr isotope ratios in crude oil after MAWD-PDC and solubilization are shown in Table 12. The results obtained after both sample preparation methods were in good agreement. However, a small difference in the ^{87}Sr/^{86}Sr ratio exceeding the uncertainty was observed between the two methods for sample C, possibly due to homogeneity and/or sampling problems. This sample also presented the lowest Sr concentration between the evaluated crude oil samples, which can also be a reason for the difference in $^{87}Sr/^{86}Sr$ ratio values. The results for NIST 1634c after digestion by MAWD-PDC were $^{87}Sr/^{86}Sr = 0.71162 \pm 0.00013$. The $^{87}Sr/^{86}Sr$ isotope ratios in crude oil ranged from 0.70993 to 0.71302. Similar to what was observed for the Mg isotopic composition, the $^{87}Sr/^{86}Sr$ ratio in crude oil is close to that of seawater ($^{87}Sr/^{86}Sr = 0.709$).[144,145] In addition, the radiogenic character of the Sr composition suggests that the crude oils were equilibrated towards more evolved rock types, enriched in Rb, e.g. alkali-rich volcanic rocks ($^{87}Sr/^{86}Sr$ up to 0.713),[105] basinal lithologies such as marine pelitic sediments ($^{87}Sr/^{86}Sr$ from 0.702 up to 0.74)[146] or even granites ($^{87}Sr/^{86}Sr$ up to 0.736).[105] Those rock types are commonly found in sedimentary basins, where crude oil is originated from. Moreover, when comparing $^{87}Sr/^{86}Sr$ ratio results obtained in this work for Brazilian crude oils ($^{87}Sr/^{86}Sr$ from 0.70993 to 0.71302) with those obtained for crude oils from Sakhalin Island, in Russia ($^{87}Sr/^{86}Sr$ from 0.70838 to 0.70911),[20] it is possible to observe that Brazilian crude oils present higher $^{87}Sr/^{86}Sr$ ratios.

For Pb isotope ratios, correction for instrumental mass discrimination was accomplished following the method described by Baxter *et al.*[127] using Tl as an internal standard.[8,123] Pb isotope ratios were obtained for crude oil samples after MAWD-PDC only, as the solubilization method was not suitable for Pb recovery. The Pb concentration in the crude oil samples analyzed in this work was very low (from 0.059 to 0.203 µg g^{-1}). Dilution of the purified Pb samples and NIST SRM 981 to 15 µg L^{-1} of Pb was needed to have enough volume for MC-ICP-MS measurements. NIST SRM 997 Tl was added to samples and standards at a concentration of 5 µg L^{-1}. In order to measure ^{202}Hg and ^{204}Pb with sufficient precision at low concentration, the Faraday collectors L3 and L1 were connected to high-sensitivity 10^{13} Ω resistors (as shown in Table 4, section 3.1). Pb isotope ratios for crude oil samples and NIST 1634c are shown in Table 12.

The $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios in the samples ranged from 17.74336 to 18.95599, from 15.58007 to 15.67888 and from 37.52644 to 38.55713, respectively. These ratios are in range with those reported in the literature for crude oil samples from different origins ($^{206}Pb/^{204}Pb$ from 17.16 to 20.59, $^{207}Pb/^{204}Pb$ from 15.39 to 16.33, and $^{208}Pb/^{204}Pb$ from 36.82 to 39.71).[15,17-19] Additionally, these values were also within the range observed for crude oils from the onshore Potiguar Basin, in northeastern Brazil ($^{206}Pb/^{204}Pb$ from 17.24 to 20.59, $^{207}Pb/^{204}Pb$ from 15.39 to

16.33, and $^{208}Pb/^{204}Pb$ from 36.82 to 39.71). Moreover, Pb isotope ratios in crude oil are also within the range reported for seawater.[147]

Table 12. Mg, Sr and Pb isotopic compositions of crude oil obtained by MC-ICP-MS after MAWD-PDC and solubilization.

	A		B		C	
Isotope ratio	MAWD-PDC	Solubilization	MAWD-PDC	Solubilization	MAWD-PDC	Solubilization
δ^{25}Mg, ‰	-0.66 ± 0.09	-0.64 ± 0.04	-0.65 ± 0.05	-0.62 ± 0.04	-0.35 ± 0.04	-0.36 ± 0.04
δ^{26}Mg, ‰	-1.26 ± 0.06	-1.23 ± 0.06	-1.25 ± 0.05	-1.20 ± 0.08	-0.71 ± 0.07	-0.70 ± 0.09
^{87}Sr/^{86}Sr	0.71100 ± 0.00002	0.71104 ± 0.00003	0.71237 ± 0.00004	0.71244 ± 0.00004	0.70993 ± 0.00005	0.70969 ± 0.00002
^{207}Pb/^{206}Pb	0.86074 ± 0.00002	nd	0.83544 ± 0.00011	nd	0.87808 ± 0.00009	nd
^{208}Pb/^{206}Pb	2.08997 ± 0.00011	nd	2.04759 ± 0.00030	nd	2.11496 ± 0.00023	nd
^{206}Pb/^{204}Pb	18.13495 ± 0.00070	nd	18.74347 ± 0.01335	nd	17.74336 ± 0.01846	nd
^{207}Pb/^{204}Pb	15.60946 ± 0.00096	nd	15.65897 ± 0.01042	nd	15.58007 ± 0.01570	nd
^{208}Pb/^{204}Pb	37.90145 ± 0.00339	nd	38.37898 ± 0.02570	nd	37.52644 ± 0.03850	nd

	D		E		NIST 1634c	
Isotope ratio	MAWD-PDC	Solubilization	MAWD-PDC	Solubilization	MAWD-PDC	Solubilization
δ^{25}Mg, ‰	-0.77 ± 0.08	-0.74 ± 0.02	-0.62 ± 0.08	-0.62 ± 0.04	-0.44 ± 0.02	nd
δ^{26}Mg, ‰	-1.53 ± 0.06	-1.44 ± 0.04	-1.19 ± 0.06	-1.14 ± 0.06	-0.86 ± 0.04	nd
^{87}Sr/^{86}Sr	0.71223 ± 0.00004	0.71222 ± 0.00003	0.71302 ± 0.00006	0.71304 ± 0.00003	0.71162 ± 0.00013	nd
^{207}Pb/^{206}Pb	0.83083 ± 0.00004	nd	0.82712 ± 0.00001	nd	0.82091 ± 0.00001	nd
^{208}Pb/^{206}Pb	2.04344 ± 0.00010	nd	2.03304 ± 0.00003	nd	2.02082 ± 0.00001	nd
^{206}Pb/^{204}Pb	18.86875 ± 0.00026	nd	18.95599 ± 0.00068	nd	19.09916 ± 0.00069	nd
^{207}Pb/^{204}Pb	15.67681 ± 0.00049	nd	15.67888 ± 0.00039	nd	15.67874 ± 0.00057	nd
^{208}Pb/^{204}Pb	38.55713 ± 0.00127	nd	38.53838 ± 0.00090	nd	38.59592 ± 0.00137	nd

nd: not determined

The uncertainties are 1SD for 3 replicate measurements, including sample decomposition and isolation.

4.5 FIGURES OF MERIT

The following analytical figures of merit of the proposed method for Mg, Sr, and Pb isotopic analysis of crude oil were evaluated: blank levels, precision and accuracy. The levels of procedural blanks, including sample preparation and isolation, for Mg ranged from 0.5 to 3% of the total Mg concentration in crude oil samples for MAWD-PDC and the solubilization method, and correction did not affect the Mg isotope ratios. For Sr and Pb, procedural blanks were always below 1% of the total analyte concentration. In general, lower blank values were obtained using MAWD-PDC than with the solubilization method. Possibly, the closed vessels used in the MAWD-PDC method minimized the contamination from originated the environment. On the other hand, almost all steps of the solubilization method are carried out is open vessels, which can increase contamination. Additionally, for MAWD-PDC, HNO_3 is used for crude oil decomposition, which can be obtained at a high purity grade and can be further purified in a sub-boiling system.

The intermediate precision is defined as the precision obtained within a single laboratory over a longer period of time (several months) and takes into account changes such as different analysts, reagents, instrument tuning, etc. These factors are mainly constant within a day but are not constant over a longer time period and thus behave as random in the context of intermediate precision. Because more effects are accounted for by the intermediate precision, its value, expressed as standard deviation, is larger than the repeatability standard deviation. Thus, the intermediate precision (1SD) was calculated according to Dauphas *et al.*,[148] taking into account the results obtained for the Mg in-house standard solution, the Pb in-house standard solution and the Sr isotopic reference material (NIST SRM 987) measured several times over a period of about six months. The intermediate precision for δ^{25}Mg and δ^{26}Mg was 0.04 and 0.06‰, respectively. For ^{87}Sr/^{86}Sr, ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb, the intermediate precision was 0.00004, 0.00004, 0.00012, 0.0020, 0.0021 and 0.0056, respectively. These values are similar to those reported in the literature for Mg, Sr and Pb isotopic analysis using MC-ICP-MS.[8,13,97,98,123]

The accuracy of the isotope ratio measurements by MC-ICP-MS was determined by the analysis of in-house isotopic standard solutions. Results are shown in Table 13 and are in agreement with the corresponding data reported in previous publications,[8,13,123] confirming the accuracy of the measurements. Additionally, it can be indicated that the Mg isotope ratio measurements at both dilution levels (60 and 150 µg L^{-1}) resulted in similar uncertainties. For the Mg in-house standard solution measured at 60 µg L^{-1} we found $\delta^{26}Mg$ = -0.64 ± 0.04‰, while measurement at 150 µg L^{-1} resulted in $\delta^{26}Mg$ = -0.64 ± 0.03‰. In addition, due to the absence of crude oil reference materials characterized for their metal isotopic compositions, the comparison of the results as obtained using the two parallel decomposition methods was the only approach to assess the accuracy of the proposed method.

Table 13. Mg and Pb isotopic composition of in-house standards obtained by MC-ICP-MS.

Standard	Isotope ratio	This work*	Reported	Ref.
Mg in-house	$\delta^{25}Mg$, ‰	-0.34 ± 0.03	-0.34 ± 0.05	13
	$\delta^{26}Mg$, ‰	-0.64 ± 0.04	-0.65 ± 0.09	13
Pb in-house I	$^{208}Pb/^{206}Pb$	2.15324 ± 0.00006	2.15331 ± 0.00003	8
	$^{207}Pb/^{206}Pb$	0.90407 ± 0.00002	0.90413 ± 0.00002	8
Pb in-house II	$^{208}Pb/^{206}Pb$	2.17612 ± 0.00004	2.17616 ± 0.00019	123
	$^{207}Pb/^{206}Pb$	0.92332 ± 0.00003	0.92331 ± 0.00006	123

*The uncertainties are 1SD for 3 replicate measurements.

4.6 Mg, Sr AND Pb ISOTOPE RATIO AS PROXIES FOR CRUDE OIL GEOCHEMISTRY

The variability in the isotope ratios of Mg, Pb and Sr demonstrated the relevance of carrying out such measurements for creating a database for crude oils from different parts of the world for comparative purposes. These data can then eventually be used as a tool for crude oil provenancing and the characteristics can potentially be linked to the age and formational mechanisms of different oil fields.

Combination of information on the natural variation in the isotopic composition of the target elements due to mass-dependent isotope fractionation and the occurrence of radiogenic daughters can be used to unravel both (*i*) the environment in which the elements with (a) radiogenic nuclide(s) evolved before being transferred into the oil and (*ii*) the nature of the geological processes as imprinted in the isotopic composition. Moreover, multiple isotopic signatures can be used in provenance studies.[105]

The results obtained for crude oil samples in this work demonstrate strong correlations between the Sr and Pb isotope ratios and a weaker correlation of the Mg isotopic composition with that of Sr, as can be observed in Figure 12 (A and B). The data suggest that the oil reservoir from which the samples originate underwent a stage of mixing of 2 isotopically distinct components, and the composition of the crude oils was likely established by acquiring an isotopic signature of the deposit bedrock, followed by mixing with seawater. The Mg isotopic composition of the oil sample C corresponds well to the universal value of seawater, $\delta^{26}Mg_{DSM3} = -0.83 \pm 0.11$, which is known to be homogeneous across the oceans.[142] This might be due to contamination of the oil during the extraction process, hinting towards its offshore origin.

The obtained results, with crude oil C having a heavy Mg isotopic composition and less radiogenic Sr, while the other oils (D, B, E) having a light Mg isotopic composition and more radiogenic Sr, and sample A lying in-between these values, suggest that the Mg isotopic composition of crude oil may potentially be used as a proxy of the bedrock towards which the oil equilibrated: e.g., biogenic carbonates,[143] igneous rocks.[149,150] However, the absence of a strong correlation, suggests the existence of (a) secondary process(es) causing Mg isotopes fractionation or an additional isotopically distinct reservoir.

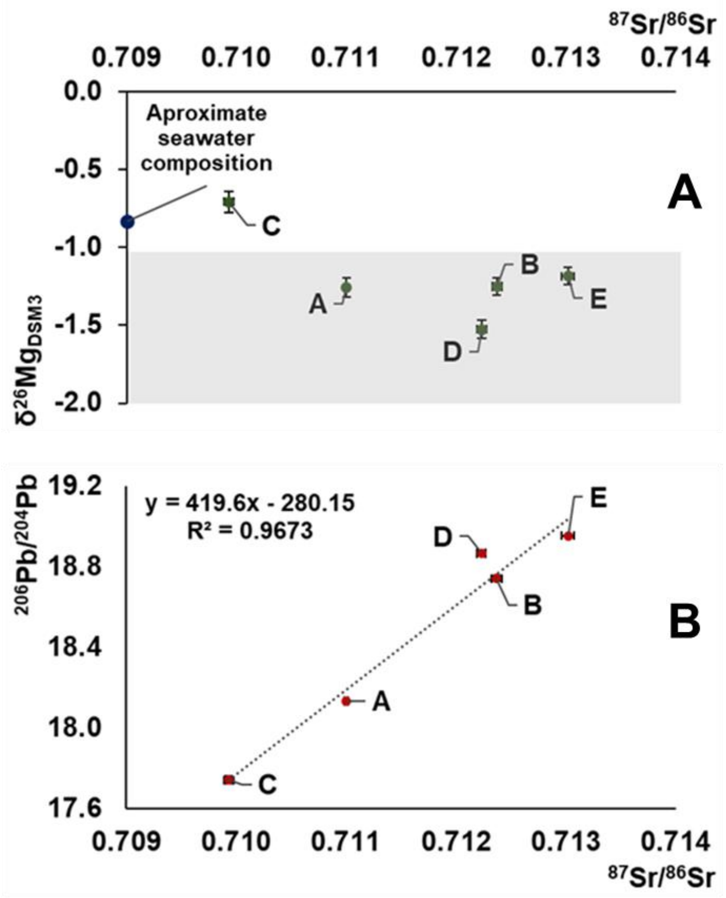

Figure 12. Representation of Mg, Sr and Pb isotope compositions of 5 Brazilian crude oils. The shaded section in plot A represents the possible isotopic composition of the deposit bedrock and (●) represents the approximate seawater composition.

5 CONCLUSION

The combination of efficient sample preparation methods, chromatographic target element isolation and MC-ICP-MS provided straightforward methods that can be used for Mg, Sr and Pb isotopic analysis of crude oils. Microwave-assisted wet digestion with a pressurized digestion cavity (MAWD-PDC) and solubilization after ASTM D4807 method were evaluated for crude oil sample preparation, and both were characterized by quantitative yields and considered suitable for Mg and Sr isotopic analysis. No statistical difference was observed between the results for Mg and Sr isotope ratios obtained using both methods. However, the determination of Pb isotope ratios was only possible after MAWD-PDC, as Pb is not recovered in the solubilization method.

A higher sample mass could be processed (up to 10 g) in the solubilization method (ASTM), which is important when considering trace elements in crude oil. In addition, both sample preparation methods are more efficient and less time-consuming in comparison with methods reported earlier in the literature (for Sr and Pb only), which rely on the use of conventional methods, such as acid digestion followed by dry ashing, liquid-liquid extraction or the use of a high-pressure asher. The use of ultra-high pressure systems with microwave radiation (as MAWD-PDC) was not yet reported for isotopic analysis of crude oil. Those systems allow for the fast heating and for digestion temperatures and pressures higher than those of conventional system. Thus, showing important advantages in comparison with the previous reported approaches. In addition, the method of solubilization of inorganic solids after the ASTM D4807 was not yet reported for elemental or isotopic analysis of crude oil. This method does not require any sophisticated equipment and the use of halogenated solvents is not required.

Isolation procedures using column chromatography were evaluated and optimized for each element. For Mg, isolation was successfully carried out using the cation exchange resin AG 50W-X8, providing quantitative yields. The use of a HF solution was not necessary for matrix elements elution from digests obtained upon MAWD-PDC. Additionally, the use of acetone was not required for matrix elements elution from solution obtained after the solubilization method, which reduces the time needed for isolation and the consumption of reagents. Moreover, it also allowed avoiding organic solvents in the purified sample. The isolation of Sr and Pb was performed using a sequential isolation protocol relying on the use of the Sr-spec resin.

The Mg-Sr-Pb isotopic composition of the crude oils was within the range observed for seawater and some rocks, sediments, and carbonates. Possibly the isotopic composition was acquired from the reservoir bedrock via leaching or equilibration followed by mixing with the seawater. The deposit bedrock with which the crude oils were equilibrated is evolved in origin, with radiogenic Sr and Pb isotopic signatures, and unlikely an igneous type due to the light Mg isotopic composition. The isotopic composition of Mg, Sr and Pb in crude oil was evidenced to carry invaluable information, while based on element concentrations, no link between the Brazilian crude oil and the source rock can be established, since changes in concentration can occur during the process of crude oil extraction.

It is important to highlight that only few works were found in the literature on Pb isotopic composition of crude oil, and only a single work was found for Sr. Additionally, the Mg isotopic analysis of crude oil is reported for the first time in this work. The analytical tools developed in this work opens a new door for oil deposit source tracing and crude oil provenancing, which was so far hampered by the lack of reliable digestion methods.

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APPENDIX

Paper published in the literature directly related to this PhD thesis:

Alessandra S. Henn, Stepan M. Chernonozhkin, Frank Vanhaecke, Erico M. M. Flores, Development of methods for Mg, Sr and Pb isotopic analysis of crude oil by MC-ICP-MS: Addressing the challenges of sample decomposition, *Journal of Analytical Atomic Spectrometry* 36 (2021) 1478-1488, doi: 10.1039/D1JA00120E
Journal impact factor (Clarivate Analytics, 2021): 4.023

Papers published in the literature during the period of the PhD:

1. Diogo L. R. Novo, **Alessandra S. Henn**, Erico M. M. Flores, Marcia F. Mesko, Feasibility of microwave-induced combustion combined with inductively coupled plasma mass spectrometry for bromine and iodine determination in human nail, *Rapid Communications in Mass Spectrometry* 34 (2020) e8675, doi: 10.1002/rcm.8675
   Journal impact factor (Clarivate Analytics, 2021): 2.419

2. Marcia F. Mesko, Diogo L. R. Novo, Vanize C. Costa, **Alessandra S. Henn**, Erico M. M. Flores, Toxic and potentially toxic elements determination in cosmetics used for make-up: A critical review, *Analytica Chimica Acta* 1098 (2020) 1-26, doi: 10.1016/j.aca.2019.11.046
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3. Matheus D. Baldissera, Carine F. Souza, Aleksandro S. Silva, **Alessandra S. Henn**, Erico M. M. Flores, Bernardo Baldisserotto, Diphenyl diselenide dietary supplementation alleviates behavior impairment and brain damage in grass carp (Ctenopharyngodon idella) exposed to methylmercury chloride, *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology* 229 (2020) 108674, doi: 10.1016/j.cbpc.2019.108674
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