

**HIGH PRECISION DETERMINATION OF TRACE ELEMENTS IN  
CRUDE OILS BY USING INDUCTIVELY COUPLED PLASMA-  
OPTICAL EMISSION SPECTROMETRY AND INDUCTIVELY  
COUPLED PLASMA-MASS SPECTROMETRY**

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A Thesis

Presented to

the Faculty of the Department of Earth and Atmospheric Sciences

University of Houston

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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By

Weihang Yang

December 2014

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## ABSTRACT

This study attempts to develop a method to precisely analyze multiple trace metal elements in crude oils by ICP-OES/ICP-MS. To eliminate spectral and polyatomic interferences caused by complex organic matrix of crude oils, oil samples were decomposed into aqueous solutions. We have studied two sample preparation techniques: combustion under high pressure and wet digestion under high pressure and temperature. A 100 ppm (wt./wt.) multi-element organo-metallic standard from Conostan, extended S21, was applied as the test standard in combustion and acid digestion. The results of combustion by ICP-OES have shown that the best recovery is about 85% for Na. For the results of wet digestion by ICP-OES, the recoveries of Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sb, Sn, and V are better than 95%, and Pb, Ti, and Zn are better than 93%.

The developed method was applied to test NIST 8505 for 47 trace elements aiming to develop it into a potential crude oil standard for multiple metal elements. Accurate concentrations of 46 elements together with V in NIST 8505 have been constrained, among them, Al, Ba, Co, Cu, Mg, Mn, Ni, and Sr have been tested by both ICP-OES/ICP-MS which showed a good agreement within analytical error range. 26 crude oil samples from Permian Basin and Fort Worth Basin, Texas, U.S., Angola, Timan Pechora Basin in Russia, and Central Sumatra Basin in Indonesia, were also tested by the developed working method for 47 trace elements. Our results indicated that the multiple trace metal contents in crude oils can be applied as a powerful tool to both upstream and downstream investigations and refining processes in the petroleum industry.

# TABLE OF CONTENTS

<b>ACKNOWLEDGEMENTS.....</b>	<b>III</b>
<b>ABSTRACT.....</b>	<b>V</b>
<b>TABLE OF CONTENTS.....</b>	<b>VI</b>
<b>LIST OF FIGURES.....</b>	<b>VIII</b>
<b>LIST OF TABLES.....</b>	<b>IX</b>
<b>Chapter 1: Introduction.....</b>	<b>1</b>
<b>1.1. Trace metals in crude oils.....</b>	<b>1</b>
<b>1.2. Sample preparation techniques.....</b>	<b>5</b>
<b>1.3. Study objectives.....</b>	<b>8</b>
<b>Chapter 2: Instrumentation and Reagents.....</b>	<b>11</b>
<b>2.1. Instruments utilized in trace element analysis of crude oils: ICP-OES, ICP-MS, and the other important devices.....</b>	<b>11</b>
<b>2.1.1. ICP-OES.....</b>	<b>11</b>
<b>2.1.2. ICP-Q-MS.....</b>	<b>16</b>
<b>2.1.3. The other important devices.....</b>	<b>17</b>
<b>2.2. Operational parameters and important instruments determinations: limit of detection (LOD), sensitivity, and background equivalent concentration (BEC)...</b>	<b>20</b>
<b>2.3. Reagents.....</b>	<b>31</b>
<b>Chapter 3: Elemental Spectrometric Data Analysis.....</b>	<b>32</b>
<b>3.1. Instrument calibrations for ICP-OES and ICP-MS.....</b>	<b>32</b>
<b>3.2. Data reduction.....</b>	<b>34</b>
<b>3.3. Results analysis.....</b>	<b>36</b>
<b>3.3.1. Interferences.....</b>	<b>37</b>
<b>3.3.2. Blank.....</b>	<b>38</b>
<b>3.3.3. Precision.....</b>	<b>41</b>

3.3.4. Accuracy.....	42
3.4. What we should pay attention to.....	42
<b>Chapter 4: Method Development.....</b>	<b>44</b>
4.1. Combustion.....	44
4.1.1. Sample preparation procedures.....	44
4.1.2. Results and discussions.....	48
4.2. Acid digestion.....	51
4.2.1. Sample preparation procedures.....	52
4.2.2. Results and discussions.....	55
4.2.3. Mineralization efficiency determined by residual carbon content (RCC) .....	57
<b>Chapter 5: Applications of the developed working method.....</b>	<b>63</b>
5.1. NIST 8505 test.....	63
5.2. 26 natural crude oil samples test.....	65
5.3. Discussions.....	72
<b>Conclusions.....</b>	<b>80</b>
<b>REFERENCES.....</b>	<b>81</b>

# LIST OF FIGURES

<b>Figure 2.1.</b> Overview of a basic ICP-OES system (Dunnivant and Ginsbach, 2009).....	12
<b>Figure 2.2.</b> Sample introduction and the subsequent reactions in the torch of an ICP system (Dunnivant and Ginsbach, 2009).....	14
<b>Figure 2.3.</b> The monochromator of an ICP-OES system (Dunnivant and Ginsbach, 2009).....	15
<b>Figure 2.4.</b> Parr oxygen bomb.....	18
<b>Figure 2.5.</b> Parr acid digestion bomb.....	19
<b>Figure 2.6.</b> Temperature-control oven used for acid digestion.....	20
<b>Figure 3.1.</b> Calibration curve of Mn (black line).....	32
<b>Figure 3.2.</b> Drift correction.....	35
<b>Figure 3.3.</b> An example of interferences for ICP-OES.....	37
<b>Figure 4.1.</b> Flow Chart for Combustion.....	44
<b>Figure 4.2.</b> Measurements of combustion of Test 1-5 by ICP-MS and Test 6 by ICP-OES.....	49
<b>Figure 4.3.</b> Flow Chart for Acid digestion.....	51
<b>Figure 4.4.</b> Measurements of combustion of Test 1-10 by ICP-OES.....	55
<b>Figure 4.5.</b> Correlation between mass loss of the sample acids mixture and $RCC_1$ within the digested solution.....	58
<b>Figure 4.6.</b> Correlation between mass loss of the sample acids mixture and $RCC_2$ within the digested solution.....	60
<b>Figure 5.1.</b> The sampled locations of the 26 natural crude oil samples.....	65
<b>Figure 5.2.</b> Ni/V ratio versus S content for organic matter types.....	71
<b>Figure 5.3.</b> Total transition metal content (Co, Cr, Cu, Mn, Ni, and V) of the 26 crude oil samples.....	76

## LIST OF TABLES

<b>Table 2.1.</b> Parameter setting of ICP-OES for aqueous samples.....	21
<b>Table 2.2.</b> Parameter setting of ICP-MS for aqueous samples.....	21
<b>Table 2.3.</b> Instruments determination parameters of ICP-MS for aqueous sample.....	27
<b>Table 2.4.</b> Instruments determination parameters of ICP-OES for aqueous sample.....	28
<b>Table 3.</b> Procedural blank of combustion (aqueous sample) by ICP-MS and acid digestion (aqueous sample) by ICP-OES.....	38
<b>Table 4.1.</b> Measurements of combustion of Test 1-5 by ICP-MS and Test 6 by ICP-OES.....	47
<b>Table 4.2.</b> Measurements of acid digestion of Test 1-10 by ICP-OES.....	54
<b>Table 4.3.</b> RCC of the digested sample solution of NIST 8505.....	57
<b>Table 4.4.</b> RCC <sub>2</sub> of the samples of crude oil reference material NIST 8505.....	59
<b>Table 5.1.</b> Measured concentrations of 47 analytes of the 8505 Test.....	61
<b>Table 5.2.</b> The sampled locations, depths, and sedimentary basins of the 26 crude oil samples.....	63
<b>Table 5.3.</b> Measured concentrations of the 47 analytes in the 26 crude oil samples by ICP-OES and ICP-MS.....	66
<b>Table 5.4.</b> Parent organic matter type, depositional environment and oil type of the 26 natural crude oil samples based on the measured concentrations of V, Ni and S.....	71

# Chapter 1: Introduction

## 1.1. Trace metals in crude oils

The information obtained from trace element concentrations in crude oils is becoming more and more important in characterizing depositional environment and source rocks, and for allowing corrective performance during crude oil processing and environmental-risk evaluation (Duyck et al., 2002). Metal elements in crude oils that have been reported using a variety of analytical techniques include Ni, V, Cu, Pb, Fe, Mg, Na, Mo, Zn, Cd, Ti, Mn, Cr, Co, Sb, U, Al, Sn, Ba, Ga, Ag, As, Sr, Au, Y, Pd, Pt, Th, La-Lu, Bi, Tl and Hg. Concentrations and ratios of trace metal elements can be used to understand oil formation, oil correlations, oil migration, maturation of organic matters, and aspects of the depositional environment of source rocks (Lewan, 1984; Elirich et al., 1985; Barwise et al., 1990; Oluwole et al., 1993; Alberdi-Genolet et al., 1999; Akinlua et al., 2007). In addition, some trace metals act as catalyst poisons during the catalytic cracking process in refining of crude oils, especially vanadium and nickel, which can be in high concentrations and cause significant corrosion of refining equipment (Akinlua et al., 2006). Thus, it is of great importance to determine the levels of these trace metals in crude oils both accurately and precisely to make decisions of whether specific metals need to be removed prior to refining. Corrosion can cause failure of refining equipment, dictates refinery maintenance schedules and refinery shutdowns, and causes direct costs of many billions of dollars per year in U.S. refineries (Nace International, 1996). Near real-time predictive corrosion information on petroleum crudes to be refined at oil

refineries may allow conditions that cause high corrosion rates to be identified and reduced and prevented prior to the refining process. This would be superior and potentially less costly to retrospective off-line monitoring, which involves monitoring methods during maintenance and shut down that measure corrosion. Obviously, this is after it has occurred and the damage to facilities has taken place.

Heavy metals commonly found in high concentrations in crude oils may enter regional drainage systems caused by on-land surface oil spills. The heavy metals are toxic at high doses. For example, Pb can damage nervous systems even at relatively low doses. Therefore, the determination of trace metals in crude oils is of great environmental and industrial importance and concern.

Trace metals present in crude oils are mostly part of porphyrins and non-porphyrins molecules. Widely distributed and highly concentrated chlorophylls are the most common precursors of porphyrins. Porphyrins include direct incorporation from biomass and formation during sedimentation (Corwin, 1959; Lewan et al., 1982). Porphyrins can be classified into two groups, one is derived from chlorophylls of algae and phytoplanktons, and are mostly present in marine depositional environments. The other one is transformed from plant chlorophylls which indicate a terrestrial origin (Treibs et al., 1936). Conversion of chlorophylls to porphyrins involves a series of reactions in the water column and during burial in sedimentation (Orr et al., 1958; Baker and Smith, 1973; Yen, 1975; Lewan, 1980). The absence of metalloporphyrins of vanadium and nickel in recent surface sediments (Baker and Hodgson, 1968; Shiobara and Taguchi, 1975) and presence in buried sediments (Louda and Baker, 1981) and thermally

immature sedimentary rocks (Hodgson et al., 1968; Shiobara and Taguchi, 1975) indicates that metallation occurs after the beginning of burial, and prior to lithification of sediments (Lewan et al., 1982). Filby (1994) directly concluded that metalloporphyrins are formed during early diagenesis and catagenesis of the source rocks, and the origin of the non-porphyrin trace elements complexes in crude oils may be primary or secondary. Catagenesis is the process that describes the cracking process that results in the conversion of organic kerogens into hydrocarbons. Cracking is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons. This is accomplished by the breaking of carbon-carbon bonds in the precursors. Rates of cracking and the end products are strongly dependent on the temperature and presence of catalysts. It results in the breakdown of a large alkane into smaller, more useful alkanes and alkenes. Simply put, hydrocarbon cracking is the process of breaking a long-chain of hydrocarbons into short ones. Primary processes refer to the release of metal complexes from kerogen during catagenesis, and generation of metal-organic complexes during mineral-organic interactions during catagenesis. Secondary processes mean the oil-mineral interaction or oil-formation water interaction during migration. Carbonaceous sedimentary rocks containing transition metals are also known to be catalytic in the conversion of hydrogen and n-alkenes into natural gas, but the source of activity in nature is unclear. As an example, the presence of transition metal catalyst Ni in crude oils has been suggested to destabilize hydrocarbons and promote their decomposition from oil to natural gas during natural cracking processes (Mango, 1996; Mango and Hightower, 1997), although no general consensus on the importance of catalysts exists (e.g., Pepper and Dodd, 1995).

A great variety of concentrations have been reported for different trace elements for a given natural crude oil. In addition, element abundances are measured using a variety of different methods, some of which lend themselves only to a narrow range of elements. In another aspect, the concentrations of a particular element in different crude oils are rarely the same providing the opportunity that suggests each oil can be fingerprinted directly, which has value in exploration, production, refining, and environmental protection.

A variety of instrumental analytical techniques, such as spectrophotometry (Milner et al., 1952), atomic absorption spectrometry (AAS) (Langmyhr and Aadalen, 1980), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Fabbe and Ruschak, 1985), inductively coupled plasma-quadrupole-mass spectrometry (ICP-Q-MS) (Lord et al., 1991), high performance liquid chromatography (HPLC) (Khuhawar and Lanjwani, 1996), gas chromatography (GC) (Delli and Patsalide, 1981), capillary electrophoreses, (Mirza et al., 2009), and X ray fluorescence spectroscopy (XRFS) (Vilhunen et al., 1997), have been used in elemental abundance determinations in crude oils. In addition, a myriad of sample preparation techniques have been used with varying degrees of success.

Indeed, much of the application field originally assigned to flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS), has been relinquished to ICP instrumental analysis techniques. Compared to these AAS techniques, both ICP-OES and ICP-MS enjoy a higher atomization temperature, a more inert environment, and the natural ability to provide simultaneous determinations for potentially up to 70 elements, which makes the ICP less susceptible to matrix

interferences. ICP also provides detection limits as low as, or even lower than GFAAS, for all but a few elements. Additionally, ICP combined technologies surpass AAS in the simplicity of operation as well (Hou and Jones, 2000).

There is little in the way of scientific publications comparing results of both ICP-OES and ICP-MS for the same crude oil samples. In fact, certification of a certain element in a certain crude oil sample requires the match of results obtained from a number of different laboratories by using diverse techniques. Our lab is equipped with both ICP-OES and ICP-MS, so we can analyze crude oil samples by using both instruments, which provides greater instrumental latitude in detection and simple sample preparation techniques.

## **1.2. Sample preparation techniques**

Crude oil is very complex in composition, viscosity, and phase. Crude oils with high organic concentration and high viscosity may influence the stability of the plasma or even cause plasma extinction. On the other hand, different phases of sample need different pretreatment for the instruments, or damage of the instruments may occur. Aqueous samples are required for ICP-OES and ICP-MS, since typically, high organic bearing samples have high content of carbon, which can deposit on, and clog the nebulizer and plasma tube of the ICP-OES, and the nebulizer, plasma tube, and sampler cone of the ICP-MS. This can result in instability or even extinction of the instrument plasma.

Four methods have been mainly used in sample preparation of analyzing high organic matrix crude oil samples: 1) mineralization directly by acid digestion, 2)

mineralization by dry ashing/combustion followed by acid digestion, 3) direct crude oil introduction after dilution with organic solvent, and 4) emulsion/micro-emulsion.

Mineralization refers to the procedure of destroying the organic structures by acid digestion/oxidization, dry ashing or combustion, so that the organic samples can be introduced into the instrument in inorganic form. During mineralization, hydrocarbons are oxidized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This can remove or minimize the polyatomic and spectrometric interferences caused by the complex organic matrix in crude oils, and avoid carbon deposition on the sampler and skimmer cones which may cause clog and plasma instability or even extinction.

For combustion/dry ashing, relatively large amounts of sample can be treated using Parr oxygen combustion bombs (1 g). Organic structures can be completely destroyed (hydrocarbons are oxidized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) via burning, so the analytical difficulties resulting from the complex organic interferences and differences in viscosity between samples and standards can be minimized. However, this method is not frequently used because it risks explosion. In addition, sample loss may occur during burning due to the uncontrollable formation of volatile species. Very few data have been reported using the combustion method for metal elements content in crude oils.

Acid digestion consists of open vessel acid digestion or closed vessel acid digestion under high temperature and high pressure. The former can be time consuming (up to several days for complete decomposition) and large amounts of reagents are needed (e.g., 10 ml of acid per 0.5 g of sample), which risks sample contamination even when reagents

grades are carefully double distilled. Additionally, it may also suffer the problem of loss of volatile elements. The latter closed vessel technique is much more efficient in decomposition, which can be done in a relatively short time, and only small amount of acid is required. This technique has also been reported to be safer, and it minimizes the contamination of samples, volume of reagents and analyte loss, (Ozcan and Akman, 2005; Trindade et al., 2006).

Direct introduction is becoming the most widely used technique in the industry. Many attempts have been made to avoid plasma overload or carbon deposition on the sampler and skimmer cones and the ICP torch, which can be summarized into optimization of the operating conditions and development of the instruments. The operation of this technique is simple and safe. What is more, direct introduction can save a lot of time because analysts do not need to spend tens of hours on sample decomposition. However, there are still some problems that need to be addressed. Large sample dilution ( $\times 100$ ,  $\times 1000$ ) is the first, especially when heavy crude oils need to be analyzed, which hamper the analysis of ultratrace elements because low analyte concentrations fall below detection limits. It also results in a smaller range of elements capable of being analyzed because of low concentrations. The second one is the differences between sample and standard matrices, especially difference in viscosity. Thus standard addition calibration method or matrix matching is necessary, which is time-consuming and impractical for high sample throughput. Furthermore, memory effects impose the long rinsing times which limit sample throughput (Ortega et al., 2013). And some crude oils suffer from solubility issues.

An emulsion or micro-emulsion is a three component system, which includes two stirred immiscible liquids and a co-solvent or surfactant which allows the three component system to be homogeneous and stable for a long term (Koen et al., 2007) (Pelizzeti and Pramauro, 1985). An emulsion or micro-emulsion can be obtained either water in oil (w/o, droplets of water in oil) or oil in water (o/w, droplets of oil in water). This technique enables the utilization of aqueous standards for instruments calibration without the need of sample mineralization, which is simple and inexpensive. Additionally, the viscosity and organic load of the system are reduced considerably due to the homogeneity and stabilization of the oil micro-droplets in water (Khuhawar et al., 2012).

### **1.3. Study objectives**

The main objective of this study is to develop a sample preparation method for crude oil samples for high precision determination of trace elements in crude oils by using both ICP-OES and ICP-MS. These instruments are valuable tools in minor, trace and ultratrace analysis of crude oil for the petroleum industry in both upstream and downstream applications (Sanabria Ortega et al., 2013). Currently, the National Institute of Standards and Technology (NIST) 8505 is the only large volume and available reference material for metal content in natural crude oils, but unfortunately only has an uncertified concentration of  $390 \pm 10$  ppm (wt./wt.) for V provided by NIST. Well certified synthetic oil standards are available (e.g., the 100 ppm (wt./wt.) multielement organometallic standard from Conostan, extended S21). The absence of well certified crude oil standard

for metal elements has seriously hampered research related to adequate techniques of multielement sample analysis. Thus, the developed working method was applied to test the NIST 8505 for a variety of metal elements aiming to develop it into a potential natural crude oil standard for multiple metal elements. Additionally, the validated sample preparation technique has also been used in determining concentrations of Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Si, Sm, Sr, Th, Ti, Tm, U, V, Yb, Zn, and Zr, 47 analytes totally, in 26 natural crude oil samples sampled from Permian Basin and Fort Worth Basin of Texas, U.S., Angola, Timan Pechora Basin of Russia, and Central Sumatra Basin of Indonesia.

Combustion and closed vessel acid digestion were tested in our study. Compared to open vessel acid digestion, closed vessel acid digestion has a higher reacting temperature and pressure and is more efficient in sample decomposition and rapid. In addition, it is less possible for closed vessel acid digestion to risk contamination or sample loss than open vessel acid digestion. Closed vessel acid digestion also avoids using large amounts of reactants.

We did not introduce direct introduction of samples with organic solvents due to the fact that this method requires large amounts of organic solvents as dilution matrix and rinsing solution, which is so expensive that it is not an ideal sample preparation technique for academic research purposes. In addition, the high dilution necessary make it less attractive for analyzing large numbers of trace and ultratrace elements due to detection difficulties. In other words, considering its characteristics of high detection limits, time-

saving, and money consuming, it may not be an ideal technique for oil and gas industry or research on trace and ultratrace in crude oils and fingerprinting with broader elemental detection capabilities.

## **Chapter 2: Instrumentation and Reagents**

### **2.1. Instruments utilized in trace element analysis of crude oils: ICP-OES, ICP-MS, and the other important devices**

Atomic optical spectrometry and mass spectrometry are the most commonly used methods for multi-elemental determination, among which the atomic optical spectrometry includes atomic absorption, atomic emission, and atomic fluorescence, and the mass spectrometry refers to ICP-MS. ICP-OES belongs to atomic emission.

#### **2.1.1. ICP-OES**

ICP-OES system can be divided into two parts connected to each other: the part of sample introduction and plasma generation (ICP), and the part for photon collection (OES), in which the major instruments of ICP are nebulizer, spray chamber, and torch, and monochromator and detector make up the part of OES (**Figure 2.1**). Nebulizer and spray chamber are in responsibility to make sure that only a mist of fine droplets smaller than 5  $\mu\text{m}$  of the sample solution is able to enter the torch, which will avoid the possible damage to the stability of the plasma caused by the droplets bigger than 5  $\mu\text{m}$  (**Figure 2.2**).

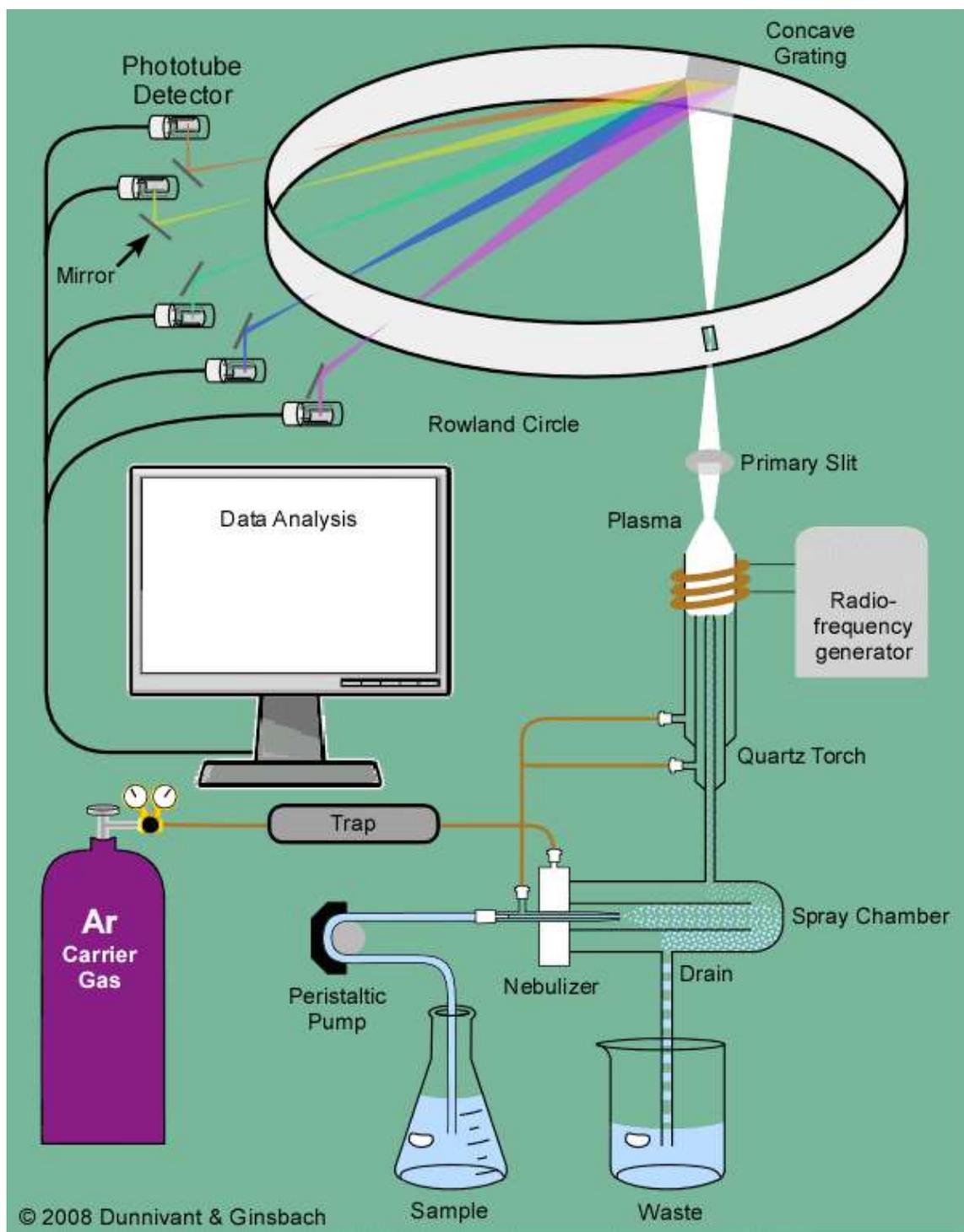


Figure 2.1. Overview of a basic ICP-OES system (Dunnivant and Ginsbach, 2009)

The torch is used to create and sustain a plasma that is a gaseous mixture of cations and electrons with a neutral charge. Cations and electrons are generated from ignition of the entered sample solution and keep moving upward until cooled, which can be divided into three stages: desolvation (vaporization of the solvent), atomization, and ionization. Argon gas flows inside the concentric channels of the ICP torch. The radio-frequency (RF) load coil is connected to a radio-frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma. Heated by the radiofrequency (RF) generator, the plasma typically has a temperature up to 6,000-10,000 K. Upon entering the plasma, solvent of samples will evaporate, and the compounds of salts form. After, these compounds decompose as they move further to the part with a higher temperature. As moving further to the hotter part, the valence electrons and atoms will be excited. The excited atoms emit photons when exiting the plasma to be cooled, and these photons will be detected by certain detectors.

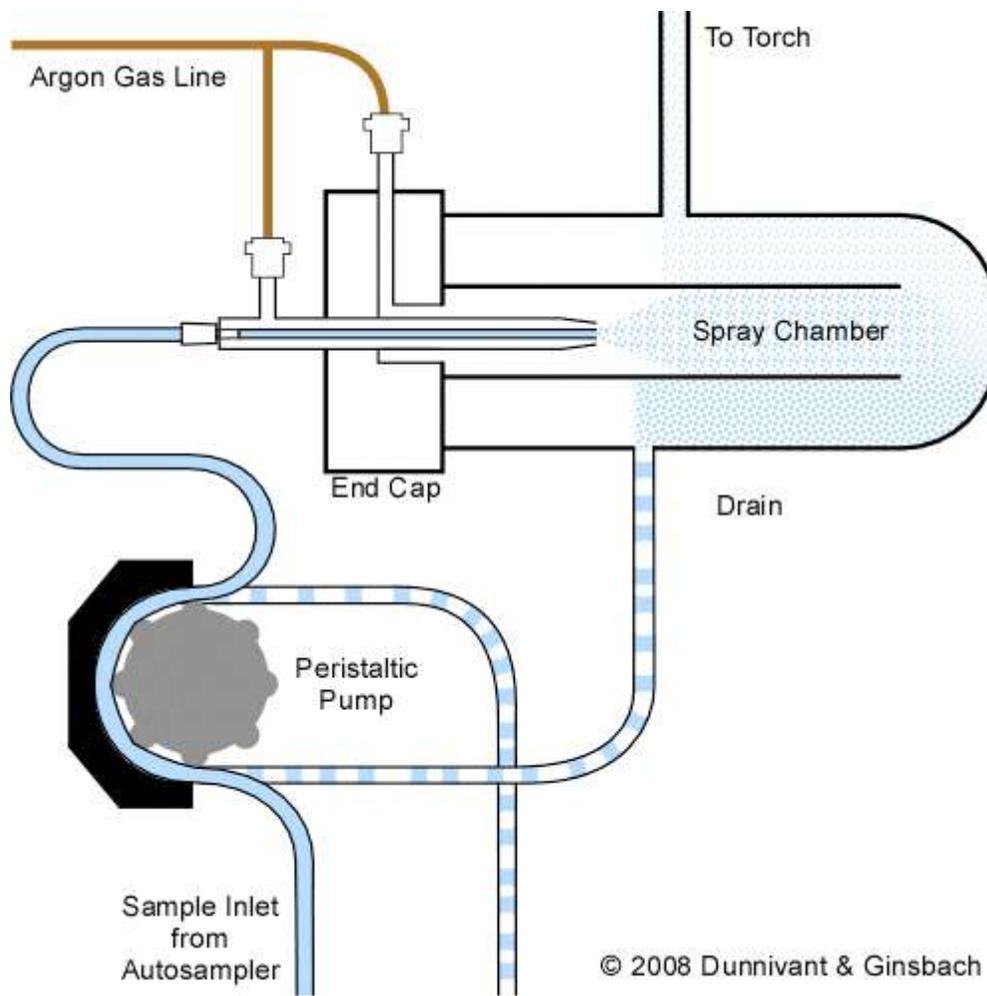


Figure 2.2. Sample introduction and the subsequent reactions in the torch of an ICP system (Dunnivant and Ginsbach, 2009)

The OES system is equipped with a sequential monochromator to separate different types of emitted photons by wavelengths, and then detects the light of the same wavelength with a single detector (**Figure 2.3**), which can be assisted by a grating system to direct the photons of different wavelengths to a specific slit to be detected by a detector, due to which multielements can be detected at the same time.

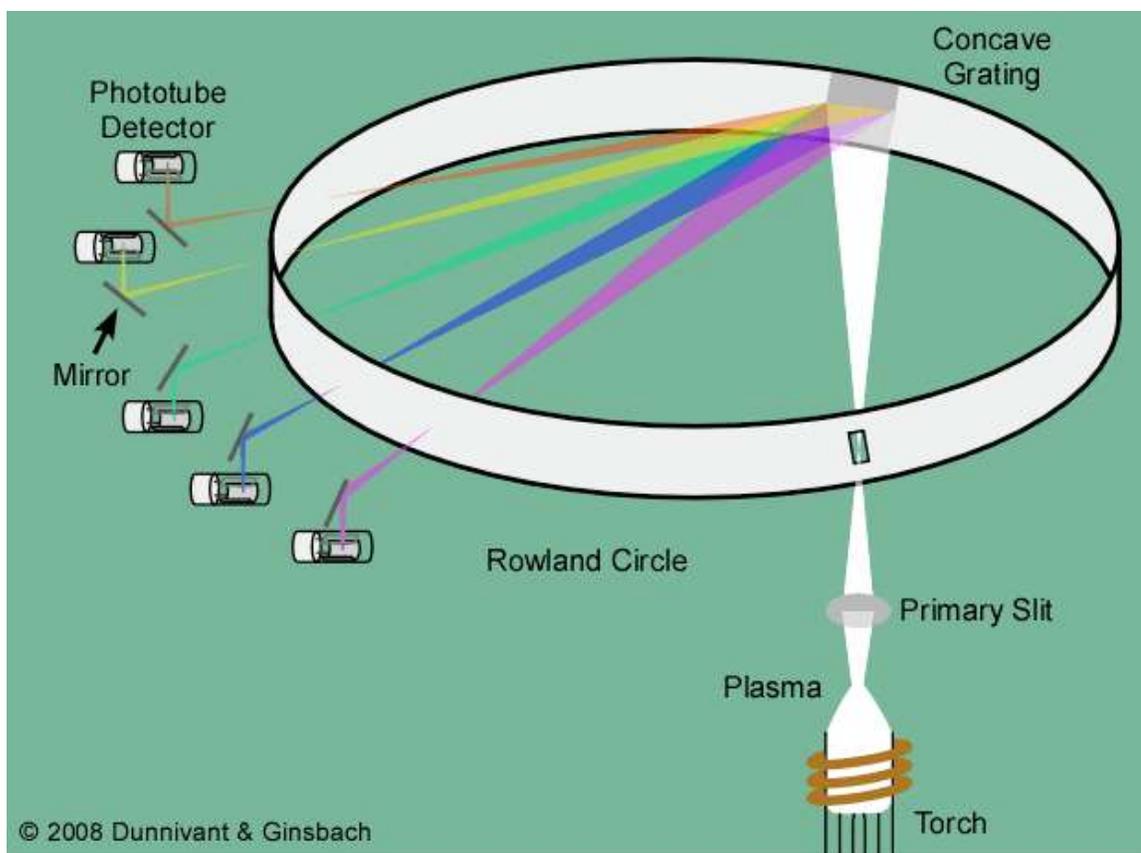


Figure 2.3. The monochromator of an ICP-OES system (Dunnivant and Ginsbach, 2009)

Then, the ICP-OES transforms the wavelength signal to electronic signal, which is the raw data used to calculate the concentrations of the elements. Generally speaking, the mechanism of this technique is to transform chemical signal into light signal, then transfer light signal into electric signal, and in the end build up a relationship between the intensity of electric signal and the concentration of the analyte in the sample.

The ICP-OES used in our study was an Agilent 725 model from Agilent Technologies, Inc., Santa Clara, California, U.S., equipped with a concentric, OneNeb nebulizer that is the most commonly used pneumatic nebulizer for samples containing

low concentrations of total dissolved solids, a double pass, cyclonic spray chamber, custom designed, hermetically sealed couple-charge device (CCD) detector that provides the ability to select multiple wavelengths for a given element for a single analysis, and a Sample Preparation System (SPS) 3 Auto-sampler that is the fastest-ever spectroscopy autosampler of Agilent, meeting the diverse requirements of high-throughput analytical experiments. It offers a range of productivity boosting features to decrease analysis times (CETAC Technologies).

### **2.1.2. ICP-Q-MS**

ICP-Q-MS distinguishes different elements by atomic mass. There is not much difference between the basic principles of ICP-Q-MS and ICP-OES for the ICP part. However, Instead of an optical emission spectrometer, a quadrupole mass spectrometer is employed in ICP-Q-MS. An interface region (sampler cone, vacuum region, and skimmer cone) and electrostatic lens system are in the middle of the ICP and QMS. The sampler and skimmer cones are used to sample the center portion of the ion beam coming from the plasma. After, a shadow stop blocks the light coming from the plasma. Then, the ions from the ICP source are forced into the aperture or slit of the mass spectrometer by a positively charged electrostatic lens system. Once the ions enter the mass spectrometer, they will be separated by their mass-to-charge ratio. The mass spectrometer with the quadrupole mass filter is the most commonly used. The quadrupole mass filter consists of 4 rods (approximately 1 cm in diameter and 15-20 cm long) which are arranged parallel to each other. In a quadrupole mass filter, alternating AC and DC voltages are applied to opposite pairs of the rods. These voltages are switched rapidly along with a

radiofrequency-field. The result is that an electrostatic filter is established that only allows ions of a certain mass-to-charge ratio ( $m/e$ ) pass through the rods to the detector at a given instant in time. The voltages can be switched so rapidly that the quadrupole mass filter separates up to 2,400 amu (atomic mass units) per second. Due to the extremely high speed, the ICP-MS is considered to be able to do multi-elemental analysis simultaneously” (Ruth E. Wolf, 2005).

The ICP-MS transforms the atomic mass signal to electronic signal, which is the raw data in calculating the concentrations of the elements.

The ICP-MS we used was a Varian 810 model from Varian Inc., Palo Alto, California, U.S., equipped with a concentric, OneNeb nebulizer, a cyclonic spray chamber, and an SPS 3 Auto-sampler. It is able to analyze atomic masses of different isotopes for a given element in a single run.

### **2.1.3. The other important devices**

A Parr oxygen bomb of model No. 1108 from Parr Instrument Company, Moline, Illinois, U.S. was used for combustion (**Figure 2.4**). The Parr oxygen bomb was airtight to minimize any potential sample loss and contamination and provide high pressure and a condition of combustion of pure oxygen for complete transformation of organic samples to inorganic matters.



Figure 2.4. Parr oxygen bomb

15 Parr high pressure acid digestion bombs of model No. 4749 also from Parr Instrument Company, Moline, Illinois, U.S. were used for acid digestion (**Figure 2.5**). The Parr acid digestion bomb was airtight as well to minimize sample loss and contamination and provide high pressure to the reactants in it.



Figure 2.5. Parr acid digestion bomb

A temperature-control oven of model MO1490A-1 from Lindberg/Blue M, Asheville, North Carolina, U.S. was used to provide high and constant temperature for the reactions of acid digestion (**Figure 2.6**).



Figure 2.6. Temperature-control oven used for acid digestion

## **2.2. Operational parameters and important instruments determinations: limit of detection (LOD), sensitivity, and background equivalent concentration (BEC)**

For introduction of the samples to the ICP instruments used for analysis, close attention should be paid to their preparation. In particular we need to pay close attention to parameter setting as the instruments are run. Parameter setting that concerns instruments running conditions for the analysis of crudes is stressed.

As what Table 2.1 and 2.2 indicates below, the optimum operating parameters determined for both the ICP-OES and ICP-MS are listed. These running conditions were

optimized based on tests we performed that included analyzing aqueous samples by using ICP-OES and ICP-MS, respectively.

Table 2.1. Parameter setting of ICP-OES for aqueous samples

Spray chamber	Double pass
Nebulizer	OneNeb
Power (kW)	1.2
Plasma flow (L/min)	15
Auxiliary flow (L/min)	1.5
Nebulizer flow (L/min)	0.75
Viewing height (mm)	10
Replicate read time (s)	10
Instrument stabilization delay (s)	15
Sample uptake delay (s)	45
Pump rate (rpm)	10
Rinse time (s)	60
Fast pump	Yes
Replicates	7

Table 2.2. Parameter setting of ICP-MS for aqueous samples

Spray chamber	Peltier cooled Cyclonic
Nebulizer	concentric
RF power (kW)	1.4
Plasma flow (L/min)	18
Auxiliary flow (L/min)	1.65
Nebulizer flow (L/min)	1
Sheath gas (L/min)	0.27
Sampling depth (mm)	5.5
Instrument stabilization delay (s)	10
Sample uptake delay (s)	40
Pump rate (rpm)	6
Rinse time (s)	120
Replicates	7

The most important instruments determinations in this study for instrument use are limit of detection (LOD), sensitivity, and background equivalent concentration (BEC) for both the ICP-OES and ICP-MS. These parameters allow us to determine the instrument of choice for each element analyzed based on natural concentrations likely in crude oils. This allows us to optimize method development for each instrument. The LOD is “the lowest concentration of an analyte in a sample that can be detected, but not necessarily quantified, under the stated conditions of the test” (A. Shrivastava, V. B. Gupta, 2011). Sensitivity is “the ability of a method or instrument to detect an analyte at a specified

concentration” (NR 149.03(28m)), or the number of counts per second (cps) obtained for a given concentration unit, e.g. cps/ppb.

Usually regulatory authorities have their own guidelines for LOD (definition and calculation method).

### **Basic Principles of Limit of Detection**

Instrument Detection Limit (IDL) is “the concentration of a target element equivalent to its signal, which is the smallest signal that can be distinguished from background noise by a particular instrument. The IDL should always be below the method detection limit, and is not used for compliance data reporting, but may be used for comparing the attributes of different instruments. The IDL is similar to the ‘critical level’ and ‘criterion of detection’ as defined in the literature” (Greenberg, 1992).

The U.S. Environmental Protection Agency (EPA) defines the Method detection Limit (MDL) as the "minimum concentration of substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte" (40 CFR part 136). “Statistically, the 99% confidence interval means that any substance detected at a concentration equal to the MDL is 99% likely to be present at a concentration greater than zero. It also means that there is a 1% chance that a substance detected at the MDL will be considered (falsely) ‘present’ when in reality the true analyte concentration is zero”. “Method detection limits are matrix, instrument and analyst specific and require a well-defined analytical method” (Ripp, 1996).

Limit of Detection (LOD) or detection limit, is “the lowest concentration level that can be determined to be statistically different from a blank (99% confidence). The LOD is typically determined to be in the region where the signal to noise ratio is greater than 5. Limits of detection are matrix, method, and analyte specific” (ss. NR 140.05(12) & 149.03(15)). “The LOD is approximately equal to the MDL for the purposes of laboratory certification”.

Signal to Noise Ratio (S/N) is “a dimensionless measure of the relative strength of an analytical signal (S) to the average strength of the background instrumental noise (N) for a particular sample and is closely related to the detection level. The ratio is useful for determining the effect of the noise on the relative error of a measurement. The S/N ratio can be measured a variety of ways, but one convenient way to approximate the S/N ratio is to divide the arithmetic mean (average) of a series of replicates by the standard deviation of the replicate results” (Skoog & Leary, 1992).

According to the recommendation given by the International Union of Pure and Applied Chemistry (IUPAC), the limit of detection (LOD) expressed as the concentration CL or the quantity QL is derived from the smallest measure XL that can be detected with reasonable certainties for a given analytical procedure. The value of XL is given by the equation:

$$(1) XL = X_{bl} + k s_{bl}$$

i.e, Limit of Detection = Mean Blank Measurement + Numerical factor recommended for confidence level (3) × Standard Deviation

where  $X_{bl}$  is the mean of the blank measures (electronic signal intensity, unit: c/s),  $s_{bl}$  is the standard deviation of the blank measures (electronic signal intensity, unit: c/s), and  $k$  is a numerical factor chosen according to the confidence level desired. IUPAC has also recommended a value of 3 for  $k$ , which gives a confidence level of about 98%.

Standard Methods define the MDL as: “constituent concentration that, when processed through the complete method, produces a signal with a 99% probability in ICP-MS. Hence in ICP-MS, the value of  $X_L$  can also be given as:

$$(2) X_L = X_{bl} + m CL$$

where  $CL$  is the concentration of limit of detection, and  $m$  is the sensitivity (unit: cps/unit concentration).

From equations (1) and (2), the concentration  $CL$  can be calculated by the following equation:

$$(3) CL = 3 s_{bl}/m$$

### **Basic Principles of Background Equivalent Concentration (BEC)**

At times the measures of background equivalent concentration (the concentration of matrix or procedural blank) for a certain element are higher than the limit of detection. In this case, the measures obtained from running samples which are below the BEC should be rejected, even if they are higher than the limit of detection. When the BEC is lower than the limit of detection, measures below the BEC will be shown as a negative value,

which means it cannot be detected by the instrument. In this case, whether the measures obtained from the running samples should be rejected relies on the limit of detection.

In the Bruker ICP-MS Software, the background equivalent concentration (BEC) is calculated by the following equation:

$$(4) \text{ BEC} = X_{bl}/m$$

Hence, the concentration CL can be calculated alternatively from the BEC and the % relative standard deviation (RSD) of the blank, that is:

$$(5) \text{ CL} = 3 \text{ RSD}_{\text{blank}} \text{ BEC}/100$$

$$\text{where } \text{RSD}_{\text{blank}} = 100 \text{ sb}/X_{bl}$$

Let us take Ba as an example, we conducted two test experiments Test 1 and 2 with 7 experimental replicates for each by using 71AB 1 ppm (wt./wt.) aqueous standard of Ba and 2% HNO<sub>3</sub> as matrix blank in one run. We obtained the standard deviations (SDs) of the signal intensity of Ba of the blank of both Test 1 and 2, which are 8.91 cps and 7.57 cps, respectively, and the average value of the sensitivities of the 14 experimental replicates (relative standard deviation is only 0.6), which is 163.768 cps/ppb, by using the 1 ppm (wt./wt.) standard. Then, we substituted the 8.91 cps standard deviation of Test 1 and the 163.768 cps/ppb sensitivity and the 7.57 cps standard deviation of Test 2 and the 163.768 cps/ppb sensitivity into equation (3), respectively. Then, we got LOD 1 and 2 for Test 1 and 2, respectively, which are 0.163 ppb (wt./wt.) and 0.139 ppm (wt./wt.). At last, we got the final LOD of Ba by calculating the average value of LOD 1 and 2, which is

0.151 ppm (wt./wt.). For BEC, we obtained the signal intensity of Ba of the blank of both Test 1 and 2, which are 27 cps and 19 cps, respectively. Then, we substituted the 27 cps signal intensity of Test 1 and the 163.768 cps/ppb sensitivity and the 19 cps signal intensity of Test 2 and the 163.768 cps/ppb sensitivity into equation (4), respectively. Then, we got BEC 1 and 2 for Test 1 and 2, respectively, which are 0.164 ppb (wt./wt.) and 0.116 ppb (wt./wt.). At last, we got the final BEC of Ba by calculating the average value of BEC 1 and 2, which is 0.140 ppb (wt./wt.).

The LOD, sensitivity, and BEC of each analyte for both the ICP-OES and ICP-MS under the running conditions mentioned above are listed below:

Table 2.3. Instruments determination parameters of ICP-MS for aqueous sample; AM: atomic mass; LOD: limit of detection of ICP-MS, ppb (wt./wt.); Sens.: sensitivity, cps/ppb; BEC: background equivalent concentration by 2% HNO<sub>3</sub>, ppb (wt./wt.); 39 analytes in total

Analyte	AM	LOD	Sens.	BEC
Ag	107	0.01	72121	0.03
Al	27	0.03	32179	0.27
As	75	0.16	10205	0.53
B	11	0.13	4712	0.58
Ba	137	0.02	24102	0.02
Be	9	0.004	4663	0.001
Cd	111	0.01	14184	0.002
Ce	140	0.001	199062	0.001
Co	59	0.001	81465	0.004
Cu	65	0.05	18637	0.20
Dy	163	0.003	54207	0.001
Er	167	0.001	48530	0.002
Eu	151	0.002	111364	0.001
Gd	157	0.004	37081	0.002
Hf	178	0.005	50263	0.01
Ho	165	0.0003	211787	0.0003

(continuing Table 2.3)

La	139	0.001	214500	0.0004
Li	7	0.003	25413	0.005
Lu	175	0.001	193834	0.001
Mg	24	0.02	22807	0.07
Mn	55	0.01	103647	0.06
Mo	95	0.01	22959	0.01
Nb	93	0.001	130159	0.002
Nd	145	0.01	19808	0.002
Ni	60	0.01	17062	0.07
Pb	208	0.03	57021	0.12
Pr	141	0.0005	238440	0.0002
Rb	85	0.001	127278	0.01
Sb	121	0.01	44359	0.05
Sm	147	0.001	34941	0.001
Sr	86	0.03	18993	0.37
Sr	88	0.001	161507	0.002
Th	232	0.01	97350	0.05
Ti	49	0.02	4744	0.04
Tm	169	0.0003	216385	0.0005
U	238	0.01	105343	0.03
V	51	0.02	82428	0.36
Yb	172	0.002	46933	0.002
Zn	66	0.11	38283	0.13
Zr	91	0.005	18476	0.01

Table 2.4. Instruments determination parameters of ICP-OES for aqueous sample; WL: wavelength, nm; LOD: limit of detection of ICP-OES, ppb (wt./wt.); Sens.: sensitivity, cps/ppb; BEC: background equivalent concentration by 2% HNO<sub>3</sub>, ppb (wt./wt.); 50 analytes in total

Analyte	WL	LOD	Sens.	BEC
Ag	328.068	0.9	6	0.4
Al	396.152	3.4	2.2	4.43
As	188.98	28.1	0.1	19.89
As	193.696	43.6	0.1	31.39
B	249.678	1.7	2.4	3.26
B	249.772	0.9	4.7	1.89
Ba	455.403	0.2	163.8	0.14

(continuing Table 2.4)

Be	313.042	0.1	149.4	0.16
Ca	396.847	0.1	314.3	4.34
Cd	214.439	2.7	1.5	4.08
Ce	418.659	3.5	1.9	2.59
Ce	446.021	9	3.5	5.06
Co	228.615	6.2	0.3	5.24
Co	238.892	3.8	1.2	4.59
Cr	283.563	3.8	2.1	8.78
Cu	327.395	1.9	5.3	1.75
Dy	340.78	3.2	1.8	2.68
Dy	353.171	1.5	8.8	1.36
Er	337.275	0.7	18.7	1.97
Er	349.91	0.7	6.3	1.03
Eu	397.197	0.6	21.2	0.26
Eu	420.504	0.3	45.5	0.17
Fe	238.204	1.9	2.6	1.97
Ga	294.363	12.2	0.6	11.32
Ga	417.204	14.7	0.9	25.02
Gd	335.048	0.9	4.4	0.47
Gd	342.246	1.3	4.2	1.71
Hf	263.872	2.4	2.1	7.8
Hf	264.141	7.7	0.9	5.64
Ho	339.895	5	1.8	12.27
Ho	345.6	1.1	5.6	0.73
K	766.491	46.4	0.4	75.13
La	333.749	3	4.5	8.57
La	379.477	1.9	9.5	2.1
Li	670.783	11.8	141.3	3.92
Lu	261.541	0.4	7.5	0.36
Lu	291.139	3.9	1.3	1.62
Mg	279.553	0.1	87.4	0.4
Mn	257.61	0.4	10.6	0.83
Mo	202.032	5.9	0.6	7.72
Na	588.995	2	14.3	127.63
Nb	309.417	3.1	1.7	1.61

(continuing Table 2.4)

Nb	313.078	3.8	2.7	7.19
Nd	401.224	3.2	3.5	6.88
Nd	406.108	5	2	6.31
Ni	230.299	5.2	0.6	2.47
P	177.434	42.2	0.1	27.79
P	213.618	24.7	0.1	27.23
Pb	220.353	24.2	0.2	33.08
Pr	390.843	4.9	3.2	31.98
Pr	417.939	2.8	2	2.66
Rb	780.026	57.2	0.8	347.53
S	180.669	23.8	0.1	324.11
S	181.972	41.5	0.1	41.75
Sb	217.582	20.6	0.1	56.85
Se	196.026	28.3	0.1	13.45
Se	203.985	105.2	0.03	26.73
Si	288.158	10.8	0.7	66.08
Sm	359.259	2.1	4	60.11
Sm	360.949	2.3	4.4	1.47
Sr	407.771	0.1	469	0.11
Sr	421.552	0.1	388	0.04
Ta	263.558	5.6	0.9	8.76
Ta	268.517	10.1	0.5	6.46
Th	269.242	21.3	0.2	12.63
Th	283.73	13	0.5	10.23
Ti	334.941	0.3	25.9	0.23
Tm	313.125	0.8	10.3	7.02
Tm	342.508	1.8	5.6	1.56
U	367.007	25.5	0.4	17.8
U	385.957	15.1	0.8	0.57
V	309.31	0.9	4.3	0.19
Yb	328.937	0.2	57	0.23
Yb	369.419	0.2	48.3	0.21
Zn	213.857	1	3.5	3.91
Zr	339.198	1.8	3.3	2.23
Zr	343.823	1.1	9.5	2.07

### **2.3. Reagents**

Double distilled pure HNO<sub>3</sub>, HCl, and HF were used in this study. Milli-Q water from Millipore Corporation, USA and 2% HNO<sub>3</sub> were used through all the analytical work. Deionized water was used in homogenization. Pure 8N HNO<sub>3</sub> was used as absorbing solution at the bottom of the quartz liner in combustion, and used 8N HNO<sub>3</sub> was used to rinse all the glasswares and Teflon beakers. The used 6N HCl was also used for rinsing. Pure 15N HNO<sub>3</sub> and 12N HCl were used for acid digestion of the metallo-organic standards.

## Chapter 3: Elemental Spectrometric Data Analysis

### 3.1. Instrument calibrations for ICP-OES and ICP-MS

Instrument calibration should be conducted prior to the analysis to make sure the instruments and standards are in good working conditions. In detail, a series of calibration standards with varying concentrations of a certain analyte are analyzed on the instrument. If the analyst can determine the standards precisely and accurately, analysis can be applied to real samples. If not, there could be a problem with the instrument or standards used, and investigations will be needed to the root cause.

We use a series of aqueous standards with increasing concentrations to calibrate the instruments. For ICP-OES, it is 71A, containing Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Li, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, and Zn, and 71B, containing Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr. Both 71A and 71B are with concentrations of 100 ppb (wt./wt.), 200 ppb (wt./wt.), 500 ppb (wt./wt.), 1 ppm (wt./wt.), 2 ppm (wt./wt.), and 5 ppm (wt./wt.) for each of the analytes. The matrices of 71A and 71B are 2% HNO<sub>3</sub> and 2% HNO<sub>3</sub>/trace HF, respectively. For ICP-MS, it is 71A and 71B with concentrations of 1 ppb (wt./wt.), 2 ppb (wt./wt.), 10 ppb (wt./wt.), 100 ppb (wt./wt.), and 200 ppb (wt./wt.) for each of the analytes. We build a coordinate system with electric signal intensity as the X axis, and concentration of a certain element of the aqueous standard as the Y axis. Typically, the electric signal intensity and the concentration should be linearly correlated for all standards investigated. In other words, the points of the standards' data should be

aligned almost in a straight line, which is called the calibration curve. If this is not the case, there again could be problems with your instruments or standards. We evaluate the linearity of the points of the standards by using correlation coefficient ( $R^2$ ). Correlation coefficients range from 0 to 1. The greater the value of correlation coefficient is, the more linear the points of the standards are. The correlation coefficient of an exact straight line is 1. In this paper, the correlation coefficients greater than 0.99 are treated as being linear and calibration curves are accepted. The concentrations of a certain element in the aqueous standards or oil samples can be calculated based on these calibration curves established (**Figure 3.1**).

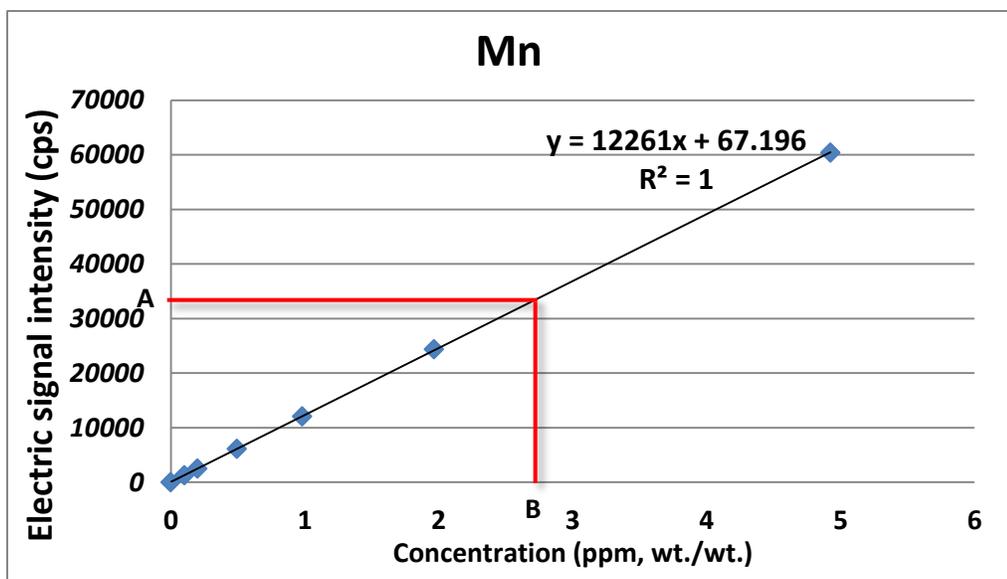


Figure 3.1. Calibration curve of Mn (black line);  $R^2 = 1$ ; When the ICP instruments report an electric signal intensity A, we can calculate and obtain its corresponding concentration B by projecting A onto the calibration curve (red line)

Linear Calibration Range (LCR), or Range of Linearity, is “the region of a calibration curve within which a plot of the concentration of an analyte versus the

response of that particular analyte remains linear and the correlation coefficient of the line is approximately 1 (0.995 for most analytes). The plot may be normal-normal, log-normal, or log-log where allowed by the analytical method. At the upper and lower bounds of this region (upper and lower limits of quantitation), the response of the analyte's signal versus concentration deviates from the line" (Ripp, 1996). In our study, the upper bounds of LCR of both ICP-OES and ICP-MS are close to  $10^9$  c/s.

### **3.2. Data reduction**

Data reduction consists of drift correction and blank correction of the raw data. When the raw intensity data are obtained, the concentration of an element in the sample solution is defined as  $C_{SA} = I_{SA} C_{ST}/I_{ST}$ , where the  $C_{SA}$  means the concentration of target element in the sample, the  $C_{ST}$  means the concentration of target element in the standard, the  $I_{SA}$  means the intensity of the electric signal of the target element in sample, and the  $I_{ST}$  means the intensity of the electric signal of target element in standard.

However, there might be drift in the sensitivity during measurements runs on multiple samples, which may be caused by the effect of changes in ambient temperature and humidity on the stability of electronic circuits (ambient induced drift), the buildup of precipitates in the sampler and skimmer cones (instrumental induced drifts) (Cheatham et al., 1993). Wangen et al. (1991) attributes many drifts to machine malfunction, which may include faulty sample transport (nebulizer, peristaltic tubing), condition of the sampler and skimmer cones, incorrect voltage settings for the lens stack, etc. Therefore, after obtaining the raw signal intensity data, analysts should conduct a drift correction by

using the data of multielement aqueous/organic standards that are applied for drift control (**Figure 3.2**). First, an approximate time period is assigned for the measurement of standard solution, and the time periods should be approximately the same, typically 20-30 min. Between these time points measurement of samples occurs and the time period for each sample should be approximately the same, typically 4-5 min. We assume that the change of the drift is linear, and the first measurement of the standard is free of drift, whose result is A and which means that the ratio to the standard (drift factor) is 1. After the first time period, we measure the standard again and get a new result B. Thus the ratio to standard is B/A. This ratio can be either higher or lower than 1, which means that the drift does exist. We assume the linear formula for drift is  $y = kx + b$ , in which “x” refers to time points and “y” refers to the ratio to standard. After doing linear regression, we get the values of “k” and “b”, by which the ratio to standard of the samples measured during the first time period can be obtained. Then we measure the standard again and derive the ratio to standard and then do the same thing to the rest of the samples, and get the second formula:  $y = k_2x + b_2$ , by which the ratio to standard of the samples measured during the second time period can be obtained. After multiplying the raw data by the ratio to standard, we get the drift corrected data of all the samples.

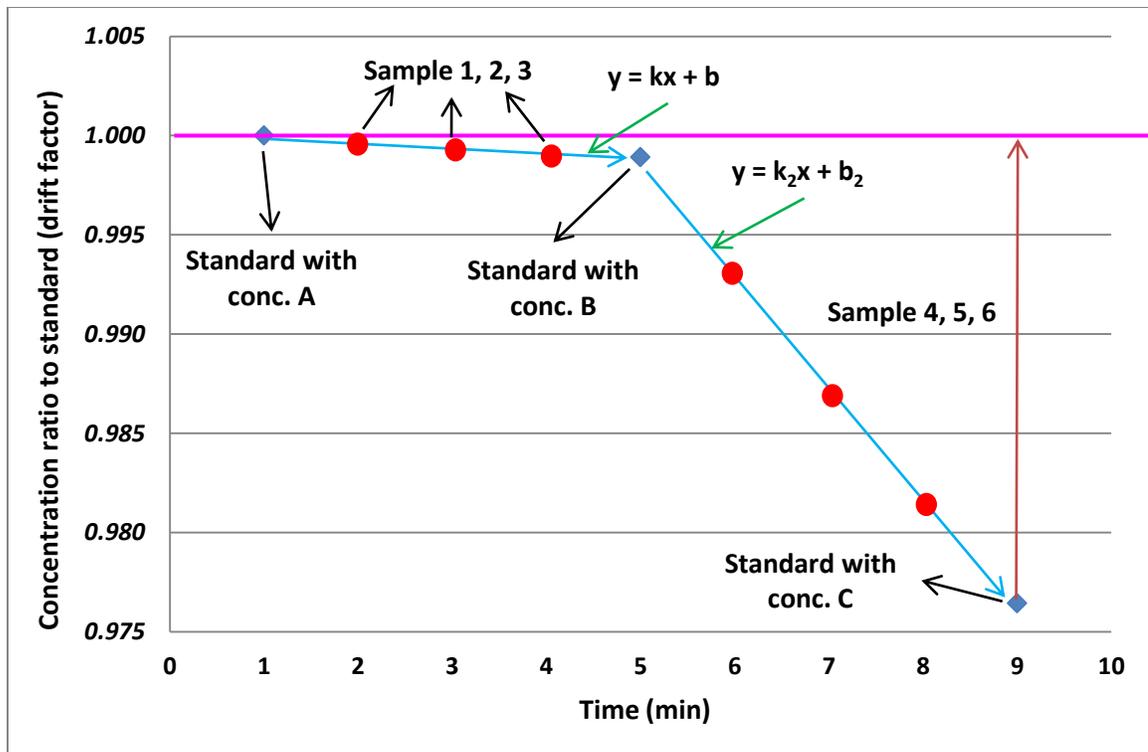


Figure 3.2. Drift correction

The signal intensity of the target elements existing in the blank is also measured. The signal intensity of the elements of interest in blank should be subtracted from the drift corrected signal intensity, because it is not generated by the target elements existing in samples.

### 3.3. Results analysis

Results analysis consists of interferences, blank and background, correlation coefficient, repeatability (precision) and accuracy analysis. Analysis can figure out what caused the incorrect data and improve the related technique based on the analysis.

### 3.3.1. Interferences

Different methods for interferences analysis have been applied to ICP-MS and ICP-OES. For ICP-MS, interferences can be caused by the noisy compounds that have the same mass as the target elements. For example,  $^{52}\text{Cr}$  can be interfered by  $^{40}\text{Ar}^{12}\text{C}$  or  $^{36}\text{Ar}^{16}\text{O}$ . By running standards with different concentrations according to the measurement range, such as 0 (blank), 2 ppb (wt./wt.) and 10 ppb (wt./wt.) in a quartz crucible, analysts can determine which element is affected by interferences caused by Ar,  $\text{N}_2$ ,  $\text{O}_2$ , sampler cone, and skimmer cone. Akinlua et al. (2008) reported that interferences can also be caused by carbon containing ions, such as  $\text{ArC}^+$ ,  $\text{CO}_2^+$ , and  $\text{C}_2^+$ , and may lead to compromise of ultra-trace analysis of certain analytes.

For ICP-OES, interferences are caused by other elements/molecules that have wavelengths equal or close to the elements of interest. Interferences can be identified on the signal plot of given wavelength (**Figure 3.3**). The Agilent 725 ICP-OES is equipped with a custom designed, hermetically sealed couple-charge device (CCD) detectors that provide the ability to select multiple wavelengths for a given element for a simultaneous analysis, thereby avoiding interferences and yielding a cost-effective, high throughput, high precision, and low detection limit analytical technique for crude oil analysis.

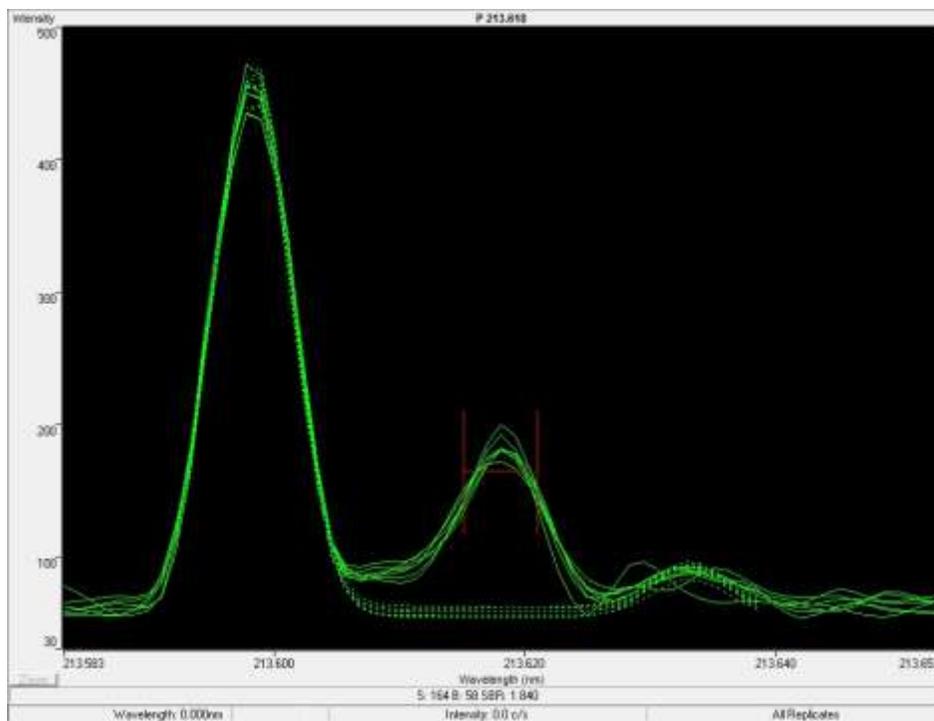


Figure 3.3. An example of interferences for ICP-OES; the peak in the middle is the signal for P at 213.618 nm wavelength, interfered by the peak of Cu at 213.598 nm wavelength on the left

In addition, interferences also can be identified by processing the data of blank and calibration standards. Take blank of 2% HNO<sub>3</sub>, the 2 ppb and 10 ppb standards as an example. The ratio of the 10 ppb and 2 ppb is 5, so if the ratio of the experimental results of the 10 ppb and 2 ppb standards is not approximately equal to 5, or the blank is close to, or equal to, or higher than either of the standards, there might be interferences.

### 3.3.2. Blank

The blank consists of matrix blank and procedural blank. Matrix blank refers to the blank of dilution matrix, such as the 2% HNO<sub>3</sub>, and procedural blank is the blank

developed from the entire experimental procedures for sample preparation without involving samples.

Table 3. Procedural blank of combustion (aqueous sample) by ICP-MS and acid digestion (aqueous sample) by ICP-OES, ppb (wt./wt.); WL: wavelength, nm; AM: atomic mass; BD: below detection limit; 50 analytes in total for ICP-OES; 39 analytes in total for ICP-MS

Analyte	WL	Acid digestion by ICP-OES	Analyte	AM	Combustion by ICP-MS
Ag	328.068	0.8	Ag	107	0.006
Al	396.152	11.3	Al	27	8.19
As	188.98	10.8	As	75	0.45
As	193.696	32.1			
B	249.678	34.8	B	11	0.93
B	249.772	1.3			
Ba	455.403	0.2	Ba	137	0.58
Be	313.042	0.2	Be	9	0.003
Ca	396.847	4.7			
Cd	214.439	0.53	Cd	111	0.01
Ce	418.659	2.4	Ce	140	0.005
Ce	446.021	6.6			
Co	228.615	5	Co	59	0.11
Co	238.892	4			
Cr	283.563	15.6			3.32
Cu	327.395	2.3	Cu	65	7.45
Dy	340.78	2.7	Dy	163	0.001
Dy	353.171	1.3			
Er	337.275	2.1	Er	167	0.0004
Er	349.91	1.3			
Eu	397.197	0.3	Eu	151	0.001
Eu	420.504	0.2			
Fe	238.204	9.3			
Ga	294.363	12.4			
Ga	417.204	31.1			
Gd	335.048	1	Gd	157	0.001
Gd	342.246	1.7			
Hf	263.872	7.8			
Hf	264.141	5.5	Hf	178	0.01
Ho	339.895	19.7	Ho	165	0.0002

(continuing Table 3)

Ho	345.6	0.9			
K	766.491	96.5			
La	333.749	8.1	La	139	0.001
La	379.477	1.7			
Li	670.783	3.9	Li	7	
Lu	261.541	0.3	Lu	175	0.0002
Lu	291.139	0.8			
Mg	279.553	1	Mg	24	3.67
Mn	257.61	0.9	Mn	55	0.48
Mo	202.032	36.7	Mo	95	0.13
Na	588.995	200.8			
Nb	309.417	1.5	Nb	93	0.03
Nb	313.078	7.7			
Nd	401.224	6.4	Nd	145	0.002
Nd	406.108	7.9			
Ni	230.299	6.2	Ni	60	3.51
P	177.434	49.5			
P	213.618	33.6			
Pb	220.353	41	Pb	208	0.4
Pr	390.843	34.8	Pr	141	0.001
Pr	417.939	2.1			
Rb	780.026	346.8	Rb	85	0.02
S	180.669	40.1			
S	181.972	53.7			
Sb	217.582	24.2	Sb	121	0.02
Se	196.026	25.6			
Se	203.985	65.1			
Si	288.158	98.7			
Sm	359.259	1.8	Sm	147	0.001
Sm	360.949	1.5			
Sr	407.771	0.1	Sr	86	0.35
Sr	421.552	0.02	Sr	88	0.09
Ta	263.558	9.2			
Ta	268.517	7.5			
Th	269.242	15.8	Th	232	0.006
Th	283.73	11.4			

(continuing Table 3)

Ti	334.941	1.3	Ti	49	0.19
Tm	313.125	7.2	Tm	169	0.0002
Tm	342.508	1.7			
U	367.007	24.3	U	238	0.001
U	385.957	BD			
V	309.31	0.2	V	51	0.52
Yb	328.937	0.2	Yb	172	0.001
Yb	369.419	0.2			
Zn	213.857	5.1	Zn	66	7.38
Zr	339.198	2.6	Zr	91	0.02
Zr	343.823	2.3			

### 3.3.3. Precision

Precision is “a measure of the random error associated with a series of repeated measurements of the same parameter within a sample. Precision describes the closeness with which multiple analyses of a given sample agree with each other, and is sometimes referred to as reproducibility. Precision is determined by the absolute standard deviation, relative standard deviation (RSD), variance, coefficient of variation, relative percent difference, or the absolute range of a series of measurements” (s. NR 140.05 (16) and Standard Methods, 18th edition), and should be calculated from more than 3 experimental replicates. Low RSD indicates good reproducibility thus a good precision.

$$RSD = \frac{100 \times SD}{Mean} \%$$

SD refers to standard deviation of the experimental replicates. Mean represents the average value of the experimental replicates.

### 3.3.4. Accuracy

Accuracy is “the closeness of the measured value to a true value” (Greenberg, 1992). It is verified in terms of recovery (RR).

$$RR = \frac{100 \times MV}{CV} \%$$

MV refers to measured value, and CV represents certified value of the standard. Therefore, in order to get good accuracy, we should assure adequate RR of the standard, i.e. approaching 100% in acceptable methods.

We used a certified method monitoring standard, the extended multi-elemental metallo-organic standard S21 from Conostan Oil Analysis Standards, Champlain, New York, U.S. with certified concentration of 100 ppm (wt./wt.) for each of the 25 analytes, Ag, Al, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sn, Ti, V, and Zn, to test the combustion and acid digestion sample preparation techniques. The measured concentration of a certain analyte can be obtained by reducing the raw data. For example, if the measured concentration is 98 ppm (wt./wt.), the accuracy of this measurement for this particular analyte will be 98/100, or 98%.

### 3.4. What we should pay attention to

Analysts improve the running condition of the instruments or the sample preparation technique according to the results analysis based on a four step procedure as follows.

- 1) Analytes that are greatly interfered should be removed from the detection list.

2) If the matrix blank is too dirty, it should be cleaned or replaced. If it is the procedural blank that is causing an abnormally high value, the sample preparation or introduction process might be subject to contamination. If the background level is too high, running condition of the instruments should be optimized, or the particular element in the sample cannot reach the detection limit of the instrument.

3) In order to get the lowest internal RSD, we should check if the samples are introduced into the machine continuously, and there are no bubbles in the introduction tubing, and the plasma is stable. If the external RSD is high, sample loss or contamination may have occurred. Attention is paid to details of each step during preparation and introduction of samples.

4) For different replicates of each method of sample preparation and introduction, typically the same amount of oxidants and dilution matrix is applied, and the running condition of the instrument is kept constant. Therefore, if the internal and external RSDs are good, but we get bad RR, this may be caused by incomplete oxidation of organic matter, volatilization or precipitation of the analytes.

During the entire development of sample preparation and introduction methods, analysts face these issues, so the decision in developing analytical methods must depend on the results analyses.

## **Chapter 4: Method Development**

We have conducted a series of comparative test experiments for combustion and acid digestion in order to find the right working method with the best precision and accuracy.

### **4.1. Combustion**

#### **4.1.1. Sample preparation procedures**

We have completed 6 test experiments in total for the development of combustion by using the method monitoring standard Conostan S21. The first 5 experiments were analyzed by using ICP-MS, and the last one was by using ICP-OES. The procedures of sample preparation appear below. We tested the experimental conditions of combustion, dissolution, acid digestion, and homogenization, to find the best combination of conditions (**Figure 4.1**). The detailed procedures are listed below.

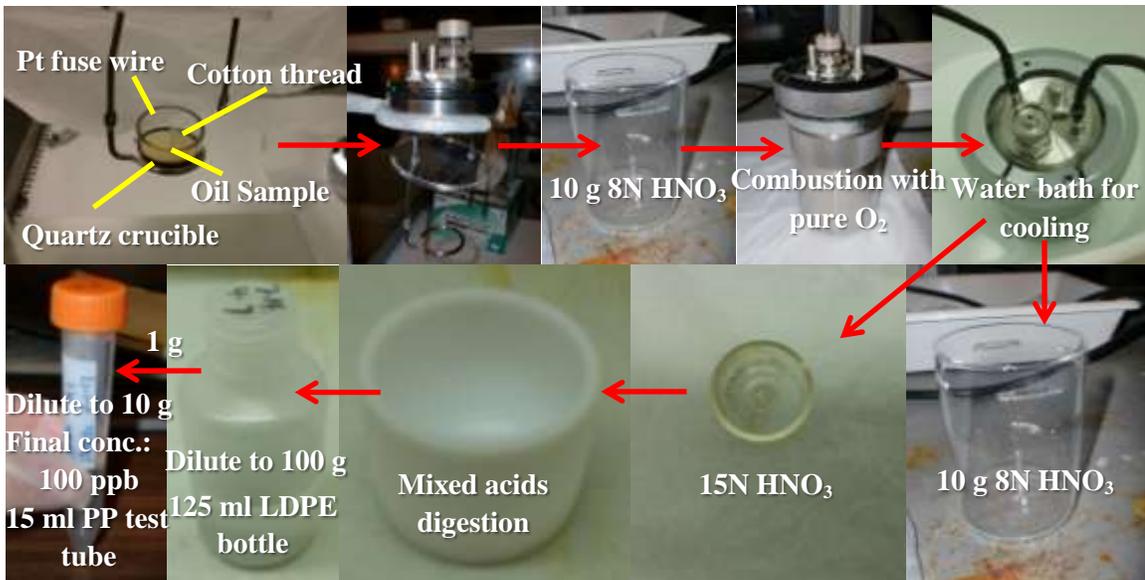


Figure 4.1. Flow Chart for Combustion; conc.: concentration

**Test 1:** Step 1: Weigh 1 g of Conostan S21 in a quartz crucible for ashing, and add 10 g of 8N nitric acid into the quartz liner as absorbing solution. A thin pure cotton thread is used to connect the sample surface and Pt fuse wire; 2: Assemble the Parr oxygen bomb and fill it up with pure oxygen by an oxygen filler until the pressure reaches 30 atm; 3: After, Put it into a water bath for cooling, and then press the button of the ignition unit. The bomb will be struck by a strong current, and the samples will be ignited inside the bomb; 4: After 10 min cooling, take it out of the water bath, dry it with Kimwipes, and release all of the gas inside the bomb very slowly to avoid any potential loss of analytes; 5: Then take out the quartz crucible, and rinse the quartz liner, the inner surface of its cover and the quartz crucible with 2% HNO<sub>3</sub>, and collect all the rinses into a 50 ml Teflon beaker; 6: Dry it down completely on a hot plate at 350 F; 7: After the solution is

dried down completely, add 10-15 ml of 2% HNO<sub>3</sub> into the Teflon beaker and heat it for 30-90 min at 350 F to pick up the samples; 8: Dilute it to about 100 ppb, and if particulates can be observed, centrifuge the solution until it gets clear.

**Test 2:** Steps 1-6 are all the same with Test 1. Step 7: Add 4 ml of 8N HCl, 1 ml of 15N HNO<sub>3</sub> and 5 ml of 24N HF into the 50 ml Teflon beaker to do the decomposition at 350 F; 8: After the solution is dried down completely, add 10-15 ml of 2% HNO<sub>3</sub> into the Teflon beaker and heat it for 30-90 min at 350 F to pick up the samples; 9: Dilute it to about 100 ppb, and if particulates can be observed, centrifuge the solution until it appears to be clear.

**Test 3:** Steps 1-4 are all the same with Test 1. Step 5: Take out the quartz crucible, then rinse the quartz liner, the inner surface of its cover and the quartz crucible with 2% HNO<sub>3</sub>, and collect all the rinses into a 50 ml Teflon beaker, and fill the quartz crucible up with 15N HNO<sub>3</sub>, then heat it on a hot plate at 350 F for 1-2 h, and collect all the rinses into the 50 ml Teflon beaker; 6: Dry it down completely on the hot plate at 350 F; 7: After the solution is dried down completely, add 10-15 ml of 2% HNO<sub>3</sub> into the Teflon beaker and heat it for 30-90 min at 350 F to pick up the samples; 8: Dilute it to about 100 ppb, and if particulates can be observed, centrifuge the solution until it appears to be clear.

**Test 4:** Steps 1-6 are all the same with Test 3, and the rest of the procedure follows step 7, 8 and 9 of Test 2.

**Test 5:** 1: Homogenize the Conostan S21 in an ultrasonic deionized water bath at about 50 °C for 20 min. The rest of the procedure follows Test 4.

**Test 6:** Step 1: Weigh 0.3 g of Conostan S21 in a quartz crucible for ashing, and add 10 g of 8N HNO<sub>3</sub> into the quartz liner as absorbing solution. A thin pure cotton thread is used to connect the sample surface and Pt fuse wire; 2: Assemble the Parr oxygen bomb and fill it up with pure oxygen by the oxygen filler until the pressure reaches 35 atm; 3: After, Put it into a water bath for cooling, and then press the button of the ignition unit; 4: After 20 min cooling, take it out of the water bath, dry it with Kimwipes, and release all of the gas inside the bomb very slowly; 5: Then, take out the quartz crucible, and rinse the quartz liner, the inner surface of its cover and the quartz crucible with 2% HNO<sub>3</sub>, and collect all the rinses into a 50 ml Teflon beaker; 6: Fill the quartz crucible with 3 ml of 12N HCl and 1 ml of 15N HNO<sub>3</sub> and heat it on the hot plate at 350 F for 1-2 h, then transfer the solution into the 50 ml Teflon beaker, and rinse the crucible with 2% HNO<sub>3</sub> and collect the rinses into the 50 ml Teflon beaker; 7: Dry down the 50 ml Teflon beaker completely; 8: Add 9 mL of 12N HCl and 3 ml of 15N HNO<sub>3</sub> into the 50 ml Teflon beaker and heat it on the hot plate at 350 F with cap on for 12 h. Check if the solution is clear, if so, Cool it down to the room temperature, and then dry it down completely. If not, go back to step 8; 9: Add 3 mL of 24N HF and 1 ml of 15N HNO<sub>3</sub> into the 50 ml Teflon beaker and heat it on the hot plate at 350 F with cap on for 12 h. This is to decompose silicon compounds. Check if the solution is clear, if so, Cool it down to the room temperature, and then dry it down completely. If not, go back to step 8; 10: Add 5 ml of 12N HCl into the 50 ml Teflon beaker and heat it on the hot plate at 350 F with cap

on for 12 h. This is to decompose fluorine compounds formed in step 9. Cool it down to the room temperature, and then dry it down completely; 11: Add 5 ml of 15N HNO<sub>3</sub> into the 50 ml Teflon beaker and heat it on the hot plate at 350 F with cap on for 12 h. Cool it down, and then dry it down completely. 12: Add 10 ml of 2% HNO<sub>3</sub> into the 50 ml Teflon beaker and heat it on the hot plate at 350 F with cap on for 30-90 min to pick up samples; 14: Dilute it to about 2 ppm.

To sum up, combinations of the conditions of the 6 test experiments are:

Test 1: Combustion only (without acid digestion); Test 2: Combustion + mixed acids digestion; Test 3: Combustion + HNO<sub>3</sub> dissolution; Test 4: Combustion + HNO<sub>3</sub> dissolution + mixed acids digestion; Test 5: Homogenization + combustion + HNO<sub>3</sub> dissolution + mixed acids digestion; Test 6: Combustion + HNO<sub>3</sub>&HCl dissolution + mixed acids digestion.

#### 4.1.2. Results and discussions

Table 4.1. Measurements of combustion of Test 1-5 by ICP-MS and Test 6 by ICP-OES; Note the isotopes (atomic mass) and spectral lines (wavelength, nm) used by ICP-MS and ICP-OES, respectively; RR: recovery, %; RSD: relative standard deviation, %

Analyte	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6		
	RR	RSD (n=5)	RR	RSD (n=5)	RR	RSD (n=2)	RR	RSD (n=5)	RR	RSD (n=5)	Analyte	RR	RSD (n=3)
Ag107	19	94.7	11	81.0	53	6.4	14	46.1	21	21.6	Ag 328.068	32	20.6
Al27	29	9.9	41	11.7	46	8.2	52	5.0	55	15.2	Al 396.152	67	3.3
B11	35	9.1	13	81.9	37	11.3	7	171.9	8	92.9	B 249.772	4	33.5
Ba137	34	12.5	30	29.2	76	1.8	63	15.4	75	13.7	Ba 455.403	71	3.5
Be9	33	9.8	40	8.2	41	5.3	45	6.3	55	16.8	Be 313.042	62	4.8
Ca44											Ca 396.847	87	10.4

(continuing Table 4.1)

Cd111	57	10.9	59	4.2	59	5.1	59	5.1	59	5.5	Cd 226.502		
Cr52											Cr 283.563	48	4.6
Cu65	54	13.3	56	9.2	67	5.0	66	5.4	69	3.7	Cu 327.395	72	1.4
Fe57											Fe 238.204	54	4.0
K39											K 766.491	68	4.3
Li7	59	9.4	66	3.9	70	3.2	67	3.5	70	3.3	Li 670.783		
Mg24	41	7.0	52	5.9	58	4.1	63	1.8	70	8.5	Mg 279.553	61	2.2
Mn55	31	11.0	41	10.9	52	6.1	58	3.5	65	8.9	Mn 257.610	63	3.5
Mo95	61	8.4	60	5.2	66	4.5	63	4.2	67	1.6	Mo 202.032	66	4.4
Na23											Na 588.995	86	8.7
Ni60	25	14.7	34	14.0	49	3.6	56	6.2	65	9.2	Ni 230.299	62	4.8
P31											P 177.434	62	6.7
Pb208	47	10.8	48	3.8	60	6.8	55	5.3	54	4.1	Pb 220.353	58	3.7
Sb121	8	26.9	8	19.3	31	1.9	22	11.1	34	17.8	Sb 217.582	35	5.5
Si29											Si 288.158	2	13.5
Sn118	6	43.2	5	12.4	28	4.1	15	34.9	26	9.3	Sn 283.998	22	2.6
Ti49	21	12.2	31	12.6	39	11.3	43	7.8	51	14.1	Ti 334.941	57	3.7
V51	62	8.6	65	3.7	71	3.2	68	3.6	73	2.7	V 309.310	63	3.6
Zn66	50	10.8	11	4.9	12	4.6	12	6.9	12	4.9	Zn 213.857	32	2.8

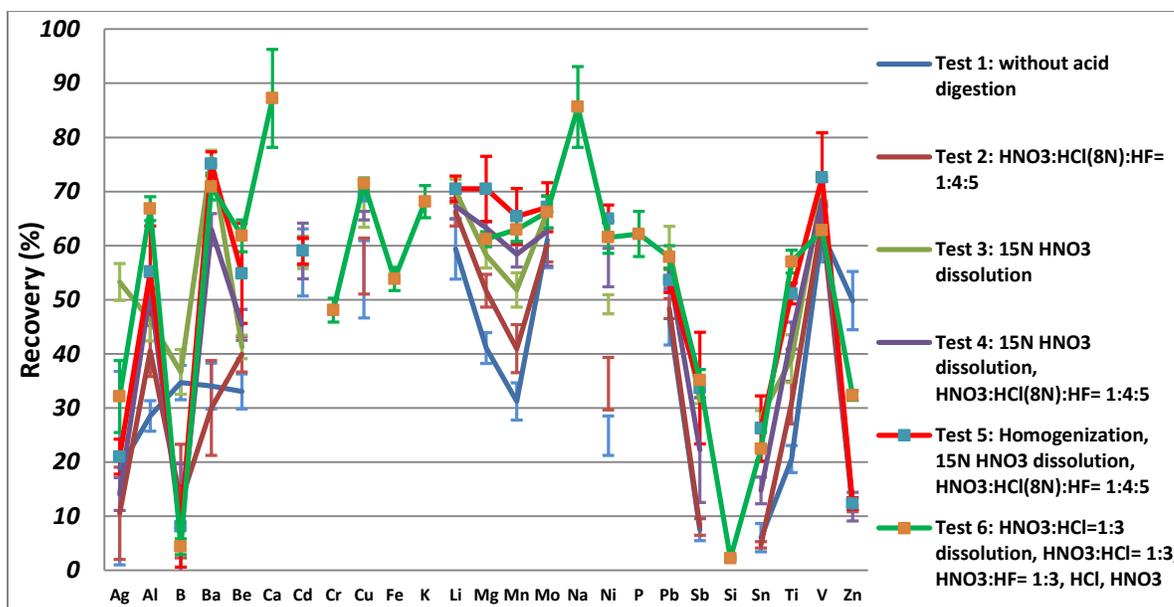


Figure 4.2. Measurements of combustion of Test 1-5 by ICP-MS and Test 6 by ICP-OES; Note combinations of the experimental replicates and differences in experimental conditions; Error bar: standard deviation, %

Among the 6 test experiments, Test 5 and 6 obtained the best recovery for most of the analytes. Thus, combination of homogenization, 15N HNO<sub>3</sub> dissolution of the crucible, and mixed acids digestion, and combination of aqua regia (concentrated HNO<sub>3</sub>:HCl = 1:3) dissolution, mixed acids digestion are the best among the 6 combinations of experimental conditions. However, no analyte can reach a recovery of 100%, and the RRs of most of the analytes are still below 80%. This has been explained by some previous work. Noble et al. (1997) has confirmed by determining Pb in burning smoke of Venezuelan crude oil that considerable portion of Pb can be lost during burning, and the more volatile of the Pb species, the more rapidly they are removed. They also extended this phenomenon to other metals and crude oil types that have the similar volatility. According to Noble's work and some analysis of gas chromatography-mass

spectrometry (GC-MS), Hammond et al. (1998) claimed that elements may exist in both of volatile form and less volatile form. The former can easily be removed from the burning samples, whereas the latter will stay behind. Sneddon et al. (2004) carried out some further investigations on the correlation between the efficiency of loss of analytes and their volatility by using Pb, Cd, Mn and Cr. They have found that it took 120-150 sec for Mn and Cr, and 30 sec for Pb and Cd to enter the smoke of burning, respectively, because Mn and Cr existed in crude oil in some chemical species that are less volatile than that of Pb and Cd species. Based on the results we obtained and previous work, we think that all of the involved analytes are present in volatile chemical forms in crude oils more or less, and these volatile species were lost in gas releases after combustion.

Another phenomenon that drew our attention is that each time I rinsed the lid of the quartz liner, there was quite a thin oil slick on it, which might not have been decomposed, thus, it cannot be detected by the instrument due to the heterogeneity of the final introduced solution, although the oil slick can be collected into the final analytical solution. This might have been caused by sputtering and splashing of the burned oil with a potential for loss of sample, because the Conostan S21 standard is a mixture of oil and water (J.L. Hammond et al., 1998). This may be the second reason for the relatively low RRs obtained in our study.

## **4.2. Acid digestion**

Due to the low recovery we obtained in the study of combustion, we investigated closed vessel acid digestion.

### 4.2.1. Sample preparation procedures

We have completed 10 test experiments in total for the development of acid digestion by using the method monitoring standard Conostan S21. All the 10 experiments were analyzed by using ICP-OES. The procedures of sample preparation appear below. We tested the experimental conditions of mass of sample, heating time and temperature, and proportion of HNO<sub>3</sub> to HCl, to find the best combination of conditions (**Figure 4.3**). The detailed procedures are listed below.

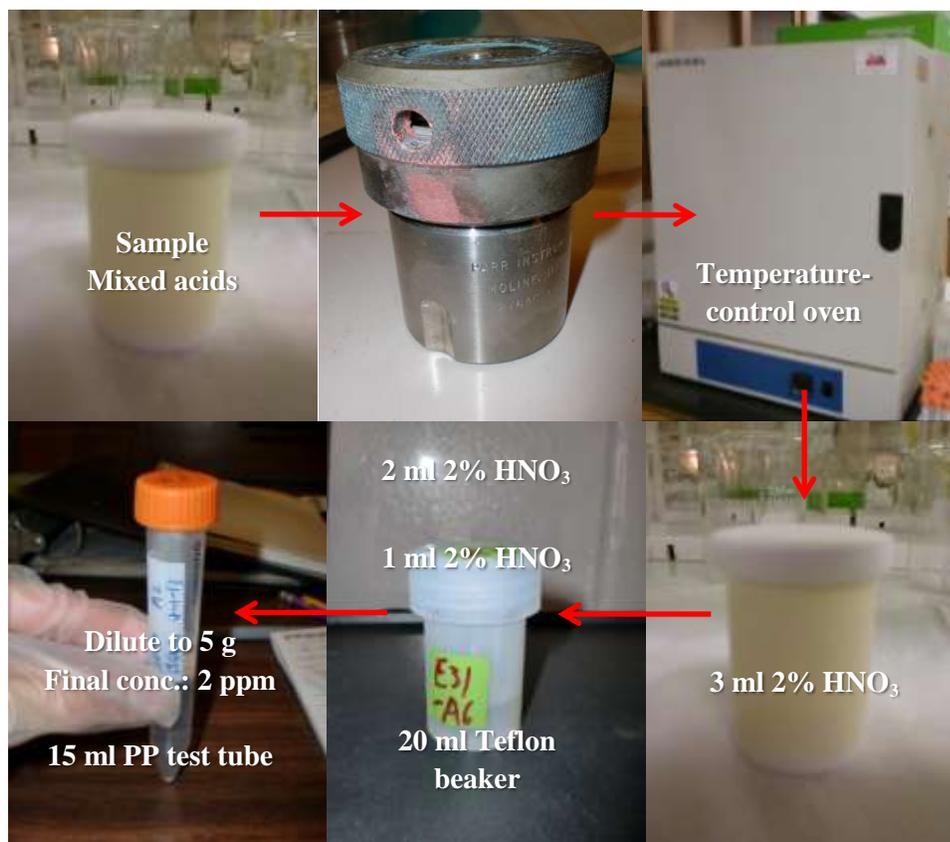


Figure 4.3. Flow Chart for Acid digestion; conc.: concentration

**Test 1:** Step 1: Weigh 0.1 g of Conostan S21 into the liner of a Parr acid digestion bomb; 2: Add 3 ml of pure 15N HNO<sub>3</sub> into the Teflon liner of the bomb; 3: Assemble the bomb; 4: Put the bomb into the mechanical oven of Lindberg/Blue M preheated to 160 °C; 5: Cook it at 160 °C for 9 h; 6: Cool it down to room temperature; 7: Open the bomb, take out the liner and clean it with Kimwipes; 8: Rinse the inner surface of the cap of the liner with 2% HNO<sub>3</sub> and collect all the rinses into the liner, then transfer the solution into a small Teflon beaker; 9: Rinse the inner wall of the liner and collect all the rinses into the small Teflon beaker as well; 10: Add 3 ml of 2% HNO<sub>3</sub> into the liner of the bomb, and heat it on the hot plate at 350 F for at least 2 h to pick residuals up; 11: Transfer the solution into the Teflon beaker; 12: Heat the beaker on a hot plate at 350 F to dry it down completely, then add 2 ml of 2% HNO<sub>3</sub> into the Teflon beaker and heat them on the hot plate at 350 F for more than 2 h with cap on to pick samples up; 13: Transfer the solution into a 15 ml test tube and rinse the beaker with 2% HNO<sub>3</sub>, then collect all the rinses into the test tube and dilute it to 2 ppm with 2% HNO<sub>3</sub> for analysis by ICP-OES (n=1), so the final solution would be 5 g.

**Test 2:** the same with Test 1 except that the mass of Conostan S21 was increased to 0.2 g (n=1).

**Test 3:** the same with Test 1 except that the mass of Conostan S21 was increased to 0.2 g and the cooking time was decreased to 7 h 40 min. The number of experimental replicates was increased to 2 (n=2).

**Test 4:** the same with Test 1 except that the cooking time was increased to 11 h (n=1).

**Test 5:** the same with Test 1 except that the cooking time was 11 h. Additionally, 2 ml of pure 12N HCl was combined with the 3 ml of pure 15N HNO<sub>3</sub> for acid digestion (n=1).

**Test 6:** the same with Test 1 except that the cooking time was increased to 15 h and 2 ml of pure 12N HCl was added (n=2).

**Test 7:** the same with Test 1 except that the cooking time was 15 h and the mixture of acid consists of 3 ml of pure 15N HNO<sub>3</sub> and 1 ml of pure 12N HCl (n=2).

**Test 8:** the same with Test 1 except that the cooking time was 11 h and 3 ml of pure 15N HNO<sub>3</sub> and 1 ml of pure 12N HCl were added as acid mixture. In addition, the cooking temperature was increased to 180 °C (n=5).

**Test 9:** the same with Test 1 except that the cooking time was 11 h and 3 ml of pure 15N HNO<sub>3</sub> and 1 ml of pure 12N HCl were added, and the cooking temperature was increased to 200 °C (n=5).

**Test 10:** the same with Test 1 except that the cooking time was 11 h and 3 ml of pure 15N HNO<sub>3</sub> and 1 ml of pure 12N HCl were combined. At step 13, we quantified the dilution by rinsing the beaker three times with 1 ml of 2% HNO<sub>3</sub>.

To sum up, combinations of the conditions of the 10 test experiments are:

Test 1: 0.1 g sample + 9 h, 160 °C heating + only HNO<sub>3</sub>; Test 2: 0.2 g sample + 9 h, 160 °C heating + only HNO<sub>3</sub>; Test 3: 0.2 g sample + 7.5 h, 160 °C heating + only HNO<sub>3</sub>; Test 4: 0.1 g sample + 11 h, 160 °C heating + only HNO<sub>3</sub>; Test 5: 0.1 g sample + 11 h, 160 °C heating + HNO<sub>3</sub>:HCl = 3:2; Test 6: 0.1 g sample + 15 h, 160 °C heating + HNO<sub>3</sub>:HCl = 3:2; Test 7: 0.1 g sample + 15 h, 160 °C heating + HNO<sub>3</sub>:HCl = 3:1; Test 8: 0.1 g sample + 11 h, 180 °C heating + HNO<sub>3</sub>:HCl = 3:1; Test 9: 0.1 g sample + 11 h, 200 °C heating + HNO<sub>3</sub>:HCl = 3:1; Test 10: 0.1 g sample + 11 h, 160 °C heating + HNO<sub>3</sub>:HCl = 3:1.

#### 4.2.2. Results and discussions

Table 4.2. Measurements of acid digestion of Test 1-10 by ICP-OES; Note the spectral lines (wavelength, nm) used by ICP-OES; T1-10: Test 1-10; RR: recovery, %; RSD: relative standard deviation, %

Analyte	T1	T2	T3a	T3b	T4	T5	T6a	T6b	T7a	T7b	T8		T9		T10	
	RR	RR	RSD (n=5)	RR	RSD (n=5)	RR	RSD (n=5)									
Ag328.068	5	8	87	4	78	18	64	19	42	89	48	56.3	76	19.3	16	45.6
Al396.152	92	98	111	115	95	94	93	93	92	94	91	6.1	95	4.4	101	1.7
B249.772	38	54	33	50	28	40	38	45	44	25	40	24.3	42	47.9		
Ba455.403	96	101	51	57	97	95	96	96	97	97	95	3.2	97	2.4	98	1.1
Be313.042	95	103	119	122	99	97	96	97	96	98	93	6.6	96	4.6	102	1.2
Ca396.847	96	100	109	113	98	100	99	99	99	99	96	3.0	98	2.5	102	1.6
Cd226.502											91	7.9	96	5.4	97	1.4
Cr283.563	98	103	118	120	100	98	97	99	97	98	97	5.3	100	4.9	104	1.6
Cu327.395	94	98	107	112	94	93	94	94	93	94	91	4.3	94	3.5	96	1.5
Fe238.204	102	101	108	111	95	97	96	98	96	98	98	9.1	102	7.5	103	2.9
K766.491	97	103	111	114	96	94	95	94	95	96	94	5.1	96	4.1	98	1.5
Li670.783															101	1.3
Mg279.553	94	101	118	119	99	97	94	96	95	98	93	7.3	98	4.9	97	1.3

(continuing Table 4.2)

Mn25 7.610	96	10 4	120	121	10 1	99	96	98	97	99	95	7.1	99	4.8	102	1.2
Mo20 2.032	88	81	83	87	90	99	96	98	98	99	96	6.3	10 0	4.0	99	1.5
Na588 .995	99	10 4	110	117	98	96	102	102	101	10 3	10 0	3.3	10 3	3.2	99	1.2
Ni230 .299	91	97	112	113	94	92	90	91	91	93	88	7.6	94	5.4	99	1.4
P177. 434	95	10 1	100	116	10 0	97	96	95	95	96	89	5.9	83	14.4		
Pb220 .353	93	10 0	70	100	10 0	97	92	93	93	95	91	9.5	97	6.0	95	1.4
Sb217 .582	35	22	9	15	29	86	89	90	89	90	84	3.9	88	4.3	97	2.8
Si288. 158	31	21	3	4	12	64	78	74	72	65	74	32.1	69	34.6	71	8.0
Sn283 .998	55	45	35	41	56	93	99	99	99	10 2	88	14.1	11 6	18.6		
Ti334. 941	88	87	69	94	88	95	96	96	96	97	93	3.7	94	3.4	94	2.2
V309. 310	91	97	109	112	94	94	92	93	93	93	90	5.7	94	3.8	106	1.2
Zn213 .857	62	66	75	76	66	65	62	63	62	64	77	7.0	81	4.9	95	1.3

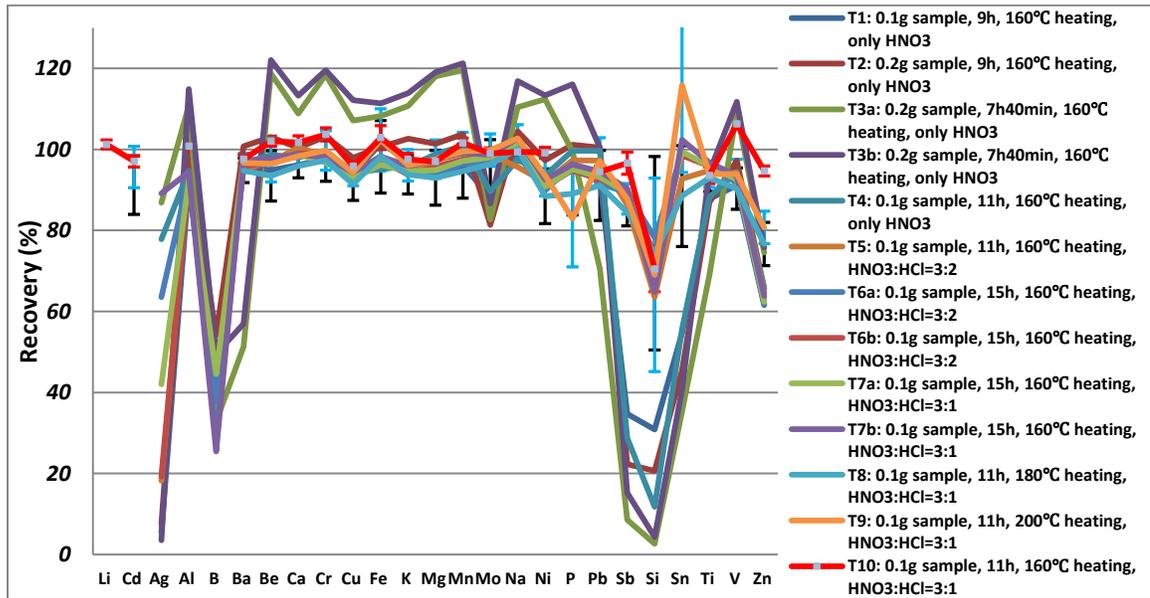


Figure 4.4. Measurements of combustion of Test 1-10 by ICP-OES; Note combinations of the experimental replicates; Error bar: standard deviation, %; Red, blue, and black error bars are for Test 10, 9, and 8, respectively; Combination of the experimental replicates of Test 10 is the best

We obtained the highest RRs and lowest RSDs from Test 10 for most of the analytes except for that of Test 3, of which RRs of most analytes are abnormally high. Thus, the method with acid digestion sample preparation technique developed in Test 10 was used as our experimental protocols for multi-elemental analysis of crude oils. The final combination of experimental conditions include 0.1 g sample, 11 h, 160 °C heating, and  $\text{HNO}_3:\text{HCl} = 3:1$ .

#### **4.2.3. Mineralization efficiency determined by residual carbon content (RCC)**

After acid digestion, organic carbons in crude oils are oxidized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . However, there are still some residual carbons left in the digested solution. In order to see if the mineralization efficiency is approximately 100%, we need to know if the residual carbon content (RCC) in digested solution is constant and falls into the reasonable range (14-18% by de Azevedo Mello Paola et al., 2009). We determined the RCC of the digested crude oil reference material NIST 8505. We conducted combustion to turn carbon into  $\text{CO}_2$  by using a CS 230 carbon sulfur analyzer that is from Leco, St. Joseph, Michigan, U.S. The generated  $\text{CO}_2$  was received by a detector, and then the mass of the carbon could be calculated out. The procedures and results are listed below.

Step 1: Weigh the 4 ml non-porous crucible that is also from Leco, and Al foil dish (should be cleaned in advance); 2: Set 5 crucibles as blanks, fill them with 1 ml of 2%  $\text{HNO}_3$  for each with pipette, and fill 1 ml of sample solutions (NIST 8505) into 24 other crucibles (All types of crucibles from Leco are intended for solid samples, so the non-

porous crucible still has tiny amount of pores. Therefore we had to fill it with liquid samples of no more than 1/4 of its capacity to reduce the pressure on the bottom to avoid sample loss); 3: Put the 29 crucibles in the Al foil dishes and weigh them to get the mass of sample solutions; 4: Put the dishes in a glass tray and cover it with clean Al foil; 5: Put the glass tray with samples in a hood for air dry overnight to remove acids; 6: Repeat step 2-5; 7: Put the glass tray with samples covered into a temperature-control oven and heat it at 37 °C overnight; 8: Weigh the crucibles and dishes to get the net mass of the residuals; 9: Combustion.

Table 4.3. RCC of the digested sample solution of NIST 8505; Total wt.: weight of the digested solution; System mass loss: mass loss of the sample acids mixture; Recovery: recovery of V

Sample	Total wt. (g)	RCC (g)	RCC (%)	System mass loss (%)	Recovery (%)
A28	1.8	0.002	0.09	15.9	98.7
C28	2.1	0.002	0.08	18.6	95.2
A29	2.1	0.001	0.05	41.2	69.0
B29	2.2	0.001	0.04	52.6	52.7
C29	2.2	0.001	0.04	51.7	54.9
D29	2.4	0.001	0.04	49.3	57.1
E29	2.3	0.001	0.05	33.6	78.8
F29	2.2	0.001	0.06	35.6	76.6
G29	2.2	0.001	0.04	48.4	58.3
H29	2.2	0.001	0.05	36.7	76.7
I29	2.3	0.002	0.07	16.1	99.4
J29	2.3	0.001	0.03	67.3	35.5
A30	2.2	0.002	0.08	13.1	100.7
B30	2.1	0.001	0.06	32.5	76.7

(continuing Table 4.3)

C30	2.1	0.002	0.08	10.5	99.1
D30	2.1	0.001	0.06	17.6	92.4
E30	2.3	0.002	0.07	10.2	99.0
F30	2.1	0.002	0.09	14.5	95.4
G30	2.1	0.001	0.07	17.9	92.8

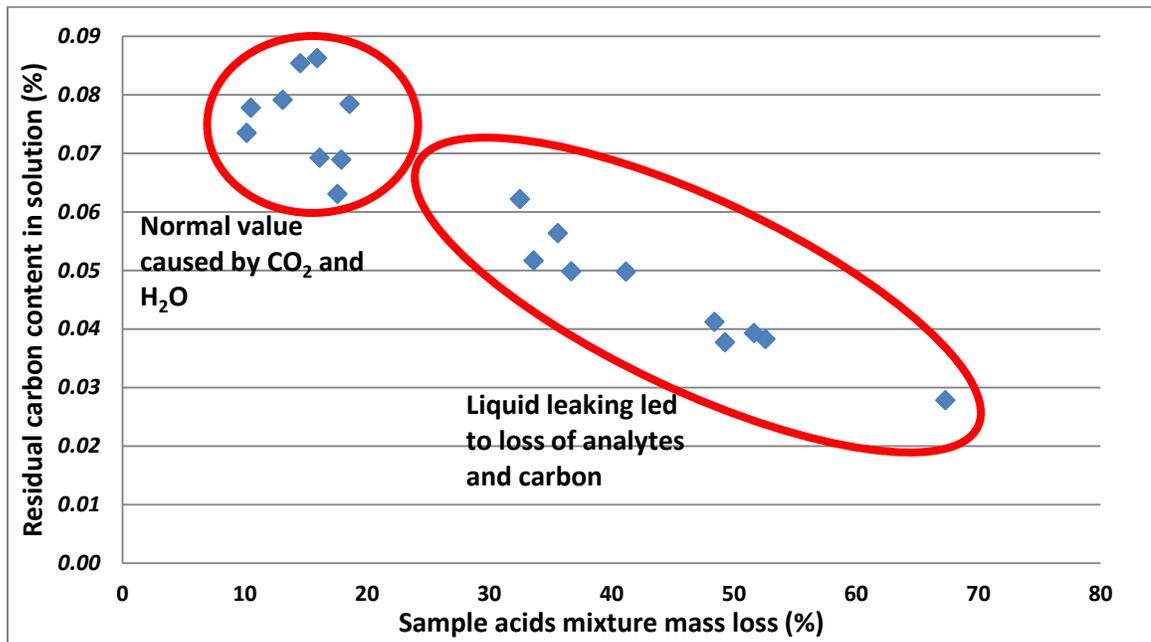


Figure 4.5. Correlation between mass loss of the sample acids mixture and  $RCC_1$  within the digested solution; Normal values caused by  $CO_2$  and  $H_2O$  are highlighted in the left red circle, and the abnormally low values highlighted in the right oval circle are caused by sample loss

We have two RCCs.  $RCC_1 = C_f (g) \times 100/M_f (g)$ , where  $RCC_1$  is the residual carbon content of the final digested solution;  $C_f$  is the mass of residual carbon in the final digested solution; and  $M_f$  is the mass of the final digested solution.

As what we can see from **Table 4.3** and **Figure 4.5**,  $RCC_1$  of the sample solution keeps decreasing with the increase of sample acids mixture mass loss.  $RCC_1$ s of the 9 samples with RR of higher than 90% range from 0.06-0.09%, and their RSD is 10.3%, which means: 1. the distribution of carbon in the digested solution is approximately homogeneous, which means that the residual carbons might be inorganic form; 2. the residual carbon content of NIST 8505 after acid digestion is relatively constant; 3. aqueous standards can be used in the determination due to such a low content of residual carbons within the digested solution.

$RCC_2$  refers to the ratio of residual carbon content to the original carbon content in the crude oils, and can be calculated by:  $RCC_2 (\%) = (C_f (\%) \times M_f (g)) / (M_s (g) \times C_s (\%))$  (Sant'Ana et al., 2007), in which  $C_f (\%)$  and  $M_f (g)$  are the concentration of carbon and mass of the final solution, respectively.  $M_s (g)$  is the mass of digested sample and  $C_s (\%)$  is the percentage of carbon in the sample. de Azevedo Mello Paola et al. (2009) mentioned that solutions obtained by microwave-assisted wet digestion of crude oil showed  $RCC_2$  about 14-18% (Recoveries of V, Ni, and S are approximately 100%). M.Y. Khuhawar et al., 2012, mentioned that the carbon contents ( $C_s$ ) of almost all crude oils range between 82-87%. According to the previous work, I recalculated the  $RCC_2$  of our work by using the 82% carbon content and 87% carbon content, respectively, and found that the  $RCC_2$ s of digests of NIST 8505 range between 15.8-18.9% for 82% carbon, and 14.9-17.8% for 87% carbon, which fall into the reasonable range of 14-18% (de Azevedo Mello Paola et al., 2009) (**Table 4.4** and **Figure 4.6**). This means that mineralization

efficiency of the developed working method with acid digestion sample preparation technique is approximately 100%.

Table 4.4.  $RCC_2$  of the samples of crude oil reference material NIST 8505

Sample	Cf (%)	Mf (g)	Ms (g)	RCC (Cs=0.82) (%)	RCC (Cs=0.87) (%)	Recovery (%)
A28	0.09	20.1	0.115	18.3	17.3	98.7
C28	0.08	20.0	0.110	17.3	16.3	95.2
I29	0.07	20.3	0.108	15.8	14.9	99.4
A30	0.08	15.4	0.083	17.9	16.8	100.7
C30	0.08	11.6	0.062	17.7	16.7	99.1
D30	0.06	13.5	0.063	16.4	15.4	92.4
E30	0.07	11.7	0.062	16.8	15.9	99.0
F30	0.09	11.7	0.064	18.9	17.8	95.4
G30	0.07	11.7	0.058	16.9	15.9	92.8

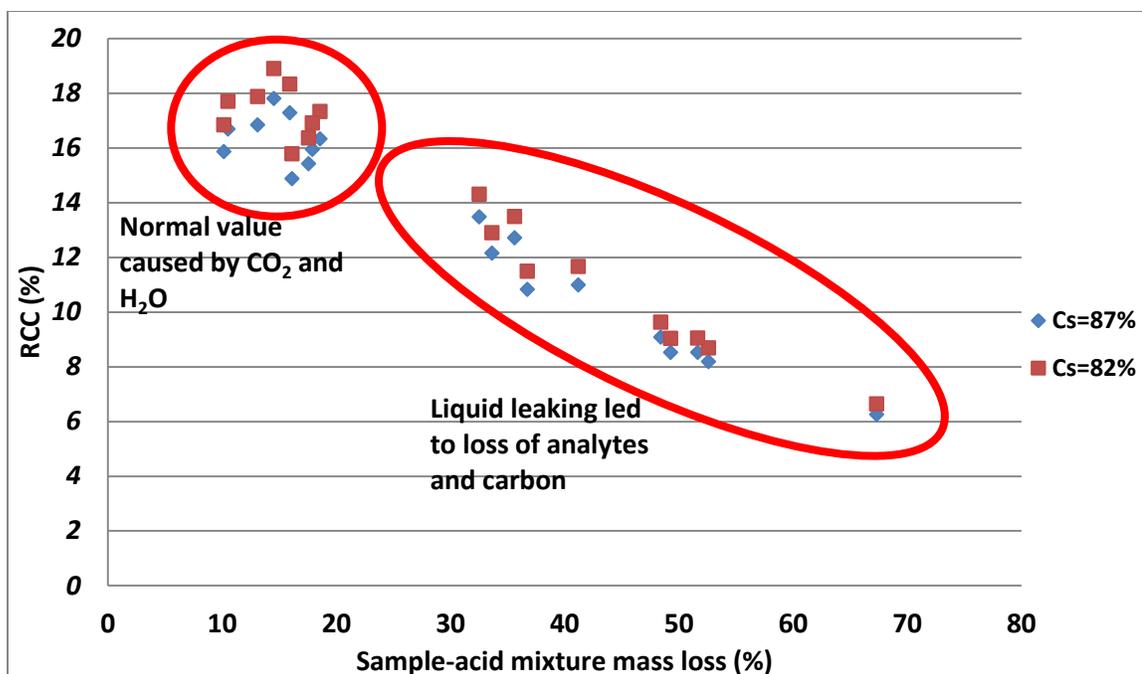


Figure 4.6. Correlation between mass loss of the sample acids mixture and  $RCC_2$  within the digested solution; Normal values caused by  $CO_2$  and  $H_2O$  are highlighted in the left red circle, and the abnormally low values highlighted in the right oval circle are caused by sample loss; Blue color: calculated in case that  $Cs = 87\%$ ; Red color: calculated in case that  $Cs = 82\%$

## Chapter 5: Applications of the developed working method

The newly developed working method with acid digestion sample preparation technique was applied to analyze 47 analytes in the test of the crude oil reference material of National Institute of Standards and Technology (NIST) 8505 and 26 natural crude oil samples sampled from Permian Basin and Fort Worth Basin in Texas of U.S., Angola, Timan Pechora Basin of Russia, and Central Sumatra Basin of Indonesia.

### 5.1. NIST 8505 test

We conducted 5 repeated acid digestions to NIST 8505, and analyzed the 5 acid digested samples by both ICP-OES and ICP-MS. The results are listed below.

Table 5.1. Measured concentrations of 47 analytes of the 8505 Test; Conc.: measured concentration, ppm (wt./wt.); RSD: relative standard deviation, %; n: number of experimental replicates; Analytes highlighted in bold and red: analyzed by ICP-OES; Analytes in black: analyzed by ICP-MS; Note the spectral lines (wavelength, nm) and isotopes (atomic mass) used by ICP-OES and ICP-MS, respectively; BD: below detection limit; Yellow color: the results by ICP-OES and ICP-MS are approximately equivalent (8 analytes); Green color: only can be detected by ICP-MS (13 analytes)

Analyte	Conc.	RSD	n	Analyte	Conc.	RSD	n
<b>Ag328.068</b>	0.054	50.3	5	Mg24	5.091	15.1	4
Ag107	0.005	38.6	2	<b>Mn257.610</b>	0.738	2.6	4
<b>Al396.152</b>	3.035	40.9	4	Mn55	0.693	3.0	4
Al27	2.932	36.6	3	<b>Mo202.032</b>	0.747	45.3	4
<b>As188.980</b>	1.384	54.9	5	Mo95	0.325	11.4	4
As75	0.197	10.1	4	<b>Na588.995</b>	17.13	31.5	5
<b>B249.772</b>	0.426	56.3	5	<b>Nb313.078</b>	BD		
B11	0.118	12.7	4	Nb93	0.009	79.2	4
<b>Ba455.403</b>	0.502	1.1	4	<b>Nd406.108</b>	BD		
Ba137	0.46	5.0	4	Nd145	0.018	16.9	4
<b>Be313.042</b>	0.031	16.8	4	<b>Ni230.299</b>	48.59	0.4	5

(continuing Table 5.1)

Be9	0.007	24.5	4	Ni60	47.01	2.3	4
<b>Ca396.847</b>	18.995	1.6	4	<b>P177.434</b>	BD		
<b>Cd214.439</b>	BD			<b>Pb220.353</b>	BD		
Cd111	0.005	53.6	4	Pb208	0.043	14.0	3
<b>Ce418.659</b>	0.087	49.6	3	<b>Pr390.843</b>	0.148	33.0	3
Ce140	0.027	12.3	4	Pr141	0.006	51.0	4
<b>Co238.892</b>	0.723	11.7	5	<b>Rb780.026</b>	BD		
Co59	0.586	2.3	4	Rb85	0.005	85.2	4
<b>Cr283.563</b>	0.71	10.7	4	<b>S180.669</b>	23912	2.0	4
<b>Cu327.395</b>	0.403	42.9	4	<b>Sb217.582</b>	BD		
Cu65	0.421	36.8	3	Sb121	0.037	46.8	4
<b>Dy340.780</b>	BD			<b>Si288.158</b>	4.389	41.1	4
Dy163	0.009	35.2	4	<b>Sm360.949</b>	BD		
<b>Er349.910</b>	0.057	68.2	5	Sm147	0.007	42.9	4
Er167	0.006	46.2	4	<b>Sr421.552</b>	0.313	4.9	5
<b>Eu420.504</b>	0.49	3.0	5	Sr88	0.271	2.5	4
Eu151	0.004	73.1	4	<b>Th283.730</b>	BD		
<b>Fe238.204</b>	6.56	16.9	5	Th232	0.027	68.3	4
<b>Gd335.048</b>	BD			<b>Ti334.941</b>	0.849	72.4	4
Gd157	0.008	35.4	4	Ti49	1.266	42.2	4
<b>Hf264.141</b>	0.295	8.9	2	<b>Tm313.125</b>	BD		
Hf178	0.014	82.8	3	Tm169	0.003	96.7	4
<b>Ho345.600</b>	BD			<b>U367.007</b>	BD		
Ho165	0.004	77.1	4	U238	0.005	57.3	4
<b>K766.491</b>	3.474	62.5	3	<b>V309.310</b>	388.3	0.7	5
Li7	0.004	111.4	3	<b>Yb369.419</b>	0.02	67.7	5
<b>La333.749</b>	0.083	56.4	5	Yb172	0.005	51.5	4
La139	0.014	23.4	4	<b>Zn213.857</b>	0.909	39.3	4
<b>Lu261.541</b>	0.067	24.5	4	Zn66	0.142	3.7	2
Lu175	0.003	96.0	4	<b>Zr339.198</b>	0.044	48.2	4
<b>Mg279.553</b>	5.766	5.1	4	Zr91	0.096	8.6	4

Accurate concentrations of 46 elements together with V in NIST 8505 have been constrained, among them, Al, Ba, Co, Cu, Mg, Mn, Ni, and Sr have been tested by both ICP-OES and ICP-MS which showed a good agreement approximately within analytical error range (RSD range).

## 5.2. 26 natural crude oil samples test

26 crude oil samples from Permian Basin and Fort Worth Basin in Texas, U.S., Angola, Timan Pechora Basin in Russia, and Central Sumatra Basin in Indonesia, were also tested by the developed working method for the 47 trace elements that were analyzed in the NIST 8505 test (Table 5.2 and Figure 5.1). The results are listed below (Table 5.3).

Table 5.2. The sampled locations, depths, and sedimentary basins of the 26 crude oil samples; None: not belong to any basin; Blank: not sure which basin the sample belongs to, because there are three basins there, Lower Congo Basin in the north, Kwanza Basin in the middle, and Namibe Basin in the south

Sample	Location	Sampled Depth (m)	Basin
H	Foard Co. TX, USA	1162-1172	none
I	Foard Co. TX, USA	1100-1104	none
D	Montague Co. TX, USA	519-746	Fort Worth Basin
E	Montague Co. TX, USA	2781-2788	Fort Worth Basin
F	Jack Co. TX, USA	1773-1777	Fort Worth Basin
G	Jack Co. TX, USA	969-988	Fort Worth Basin
P	Wise Co. TX, USA	1227-1228	Fort Worth Basin
Q	Wise Co. TX, USA	1728-1736	Fort Worth Basin
R	Grayson Co. TX, USA	2179-2180	Fort Worth Basin

(continuing Table 5.2)

S	Grayson Co. TX, USA	2123-2141	Fort Worth Basin
K	Sterling Co. TX, USA	2396-2501	Permian Basin
L	Sterling Co. TX, USA	2218-2405	Permian Basin
M	Tom Green Co. TX, USA	1435-1441	Permian Basin
N	Tom Green Co. TX, USA	1294-1295	Permian Basin
O	Irion Co. TX, USA	2641-2657	Permian Basin
T	Borden Co. TX, USA	2075-2077	Permian Basin
U	Borden Co. TX, USA	2492-2845	Permian Basin
V	Glasscock Co. TX, USA	2811-2890	Permian Basin
J	Offshore Angola	2310	
A	Offshore Angola	2566	
W	Angola	3129	
X	Angola	4277	
C	Timan Pechora Province, Russia	1088-1125	Timan Pechora Basin
B	Timan Pechora Province, Russia	1263-1265	Timan Pechora Basin
Y	Central Sumatra, Indonesia	1174-1198	Central Sumatra Basin
Z	Central Sumatra, Indonesia	1372-1386	Central Sumatra Basin

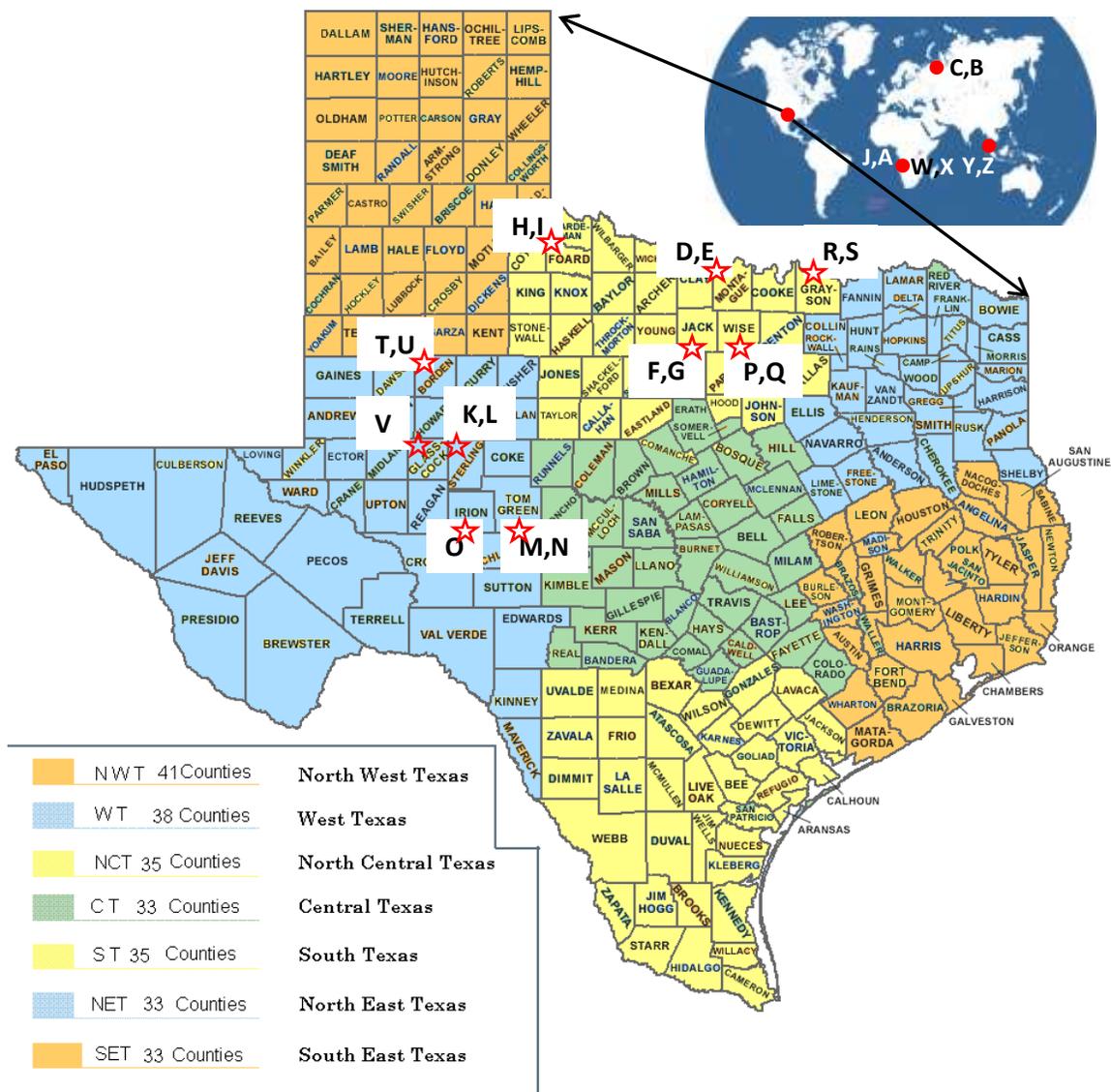


Figure 5.1. The sampled locations of the 26 natural crude oil samples

Table 5.3. Measured concentrations of the 47 analytes in the 26 crude oil samples by ICP-OES and ICP-MS, ppm (wt./wt.); Information of samples H-Z refers to Table 5.2; Analytes highlighted in bold and red: analyzed by ICP-OES; Analytes in black: analyzed by ICP-MS; Note the spectral lines (wavelength, nm) and isotopes (atomic mass) used by ICP-OES and ICP-MS, respectively; BD: below detection limit

Analyte	H	I	D	E	F	G	P	Q	R
Ag107	0.012	0.007	0.009	0.010	0.026	0.009	0.004	0.002	0.376
<b>Al396.152</b>	3.919	3.555	9.833	3.224	4.445	3.042	3.456	4.065	3.931
As75	0.160	0.150	0.181	0.218	0.117	0.180	0.225	0.177	0.135
<b>B249.772</b>	0.470	0.175	0.209	0.144	0.137	0.118	0.192	0.149	0.108
<b>Ba455.403</b>	0.023	0.016	0.034	0.041	0.019	0.013	0.032	0.030	0.013
Be9	0.002	0.003	0.002	0.001	0.002	0.002	0.002	0.001	0.002
<b>Ca396.847</b>	4.782	3.699	3.122	5.331	5.141	4.189	3.055	3.074	1.075
Cd111	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.001	0.302
Ce140	0.001	0.001	0.0005	0.008	0.001	0.001	0.001	0.0004	0.0004
Co59	0.012	0.019	0.010	0.006	0.012	0.028	0.007	0.017	0.018
<b>Cr283.563</b>	1.391	1.043	0.810	0.772	2.210	4.770	2.037	1.941	0.736
<b>Cu327.395</b>	1.958	4.605	3.710	0.839	1.423	4.156	1.875	6.437	0.703
Dy163	0.001	0.0001	0.00004	0.0001	0.0001	0.00004	0.00005	0.00003	0.00003
Er167	0.001	0.00004	0.00002	0.0004	0.00002	0.00002	0.00004	0.00003	0.00001
Eu151	0.00005	0.00004	0.00002	0.0001	0.00003	0.00002	0.00002	0.00002	0.00001
<b>Fe238.204</b>	4.053	3.374	2.894	2.805	8.445	17.979	5.779	6.455	2.775
Gd157	0.0004	0.0001	0.0001	0.096	0.0002	0.0001	0.0001	0.0001	0.0001
Hf178	0.0003	0.001	0.0005	0.006	0.0003	0.0002	0.0004	0.0004	0.001
Ho165	0.0002	0.00003	0.00001	0.0001	0.00001	0.00001	0.00001	0.00001	0.00001
<b>K766.491</b>	0.021	BD	0.030	0.049	0.015	0.024	0.001	0.027	0.011
La139	0.0005	0.0003	0.0003	0.001	0.001	0.0004	0.0004	0.0002	0.0002
Li7	0.004	0.004	0.002	0.003	0.003	0.002	0.002	0.001	0.001
Lu175	0.0001	0.00002	0.00001	0.00004	0.00001	0.00001	0.00001	0.00001	0.00001
<b>Mg279.553</b>	0.314	0.377	0.388	0.471	0.359	0.333	0.314	0.236	0.125
<b>Mn257.610</b>	0.087	0.071	0.072	0.061	0.164	0.417	0.097	0.202	0.041
Mo95	0.087	0.085	0.099	0.146	0.114	0.188	0.146	0.060	0.076
<b>Na588.995</b>	14.808	12.378	11.793	9.553	8.528	9.832	7.999	9.320	0.664
Nb93	0.005	0.004	0.005	0.005	0.006	0.008	0.002	0.001	0.005
Nd145	0.0004	0.0003	0.0002	0.218	0.0005	0.0004	0.0004	0.0001	0.0002
<b>Ni230.299</b>	6.023	11.347	2.724	1.563	1.693	5.211	1.679	5.582	7.444
<b>P213.618</b>	1.025	0.480	0.364	0.212	0.415	0.054	0.365	0.133	0.181
Pb208	0.054	0.091	0.150	0.058	0.128	0.115	0.115	0.109	0.067
Pr141	0.0001	0.0001	0.0001	0.888	0.0002	0.0001	0.0001	0.00003	0.00004
Rb85	0.001	0.001	0.001	0.004	0.001	0.001	0.001	0.001	0.001

(continuing Table 5.3)

<b>S180.669</b>	1544	2554	2117	2108	97.184	1062	1399	921	2994
Sb121	0.279	0.036	0.038	0.158	0.048	0.028	0.039	0.023	0.036
<b>Si288.158</b>	36.433	4.159	3.706	2.098	3.383	1.856	2.590	2.890	1.781
Sm147	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.00005	0.0001
<b>Sr407.771</b>	0.037	0.024	0.026	0.016	0.013	0.013	0.041	0.070	0.004
Th232	0.0002	0.001	0.0004	0.001	0.0003	0.0001	0.0001	0.0001	0.0001
<b>Ti334.941</b>	0.188	0.680	0.196	0.442	0.166	0.114	0.236	0.179	0.120
Tm169	0.001	0.001	0.0001	0.0001	0.0002	0.0003	0.0002	0.00004	0.00004
U238	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
<b>V309.310</b>	0.477	1.480	0.671	0.491	0.002	0.122	0.261	0.036	18.254
Yb172	0.001	0.0001	0.00003	0.0001	0.00004	0.00002	0.00005	0.00002	0.00004
<b>Zn213.857</b>	1.626	2.944	2.067	2.085	1.271	3.077	2.131	2.319	1.324
Zr90	0.014	0.006	0.015	0.163	0.007	0.005	0.015	0.019	0.026

(continuing Table 5.3)

Analyte	S	K	L	M	N	O	T	U	V
Ag107	0.084	0.020	0.030	0.006	0.004	0.027	0.007	0.003	0.001
<b>Al396.152</b>	2.634	2.458	1.478	12.725	1.573	3.525	4.390	11.605	2.656
As75	0.131	0.181	0.145	0.204	0.183	0.132	0.172	0.262	0.126
<b>B249.772</b>	0.111	0.126	0.101	0.100	0.099	0.458	0.109	0.117	0.439
<b>Ba455.403</b>	0.014	3.706	0.012	0.013	0.011	0.016	0.014	0.021	0.016
Be9	0.001	0.002	0.003	0.001	0.001	0.001	0.001	0.001	0.001
<b>Ca396.847</b>	1.799	6.177	2.025	2.027	1.712	1.542	2.760	6.602	2.383
Cd111	0.002	0.001	0.007	0.001	0.002	0.001	0.001	0.002	0.004
Ce140	0.0004	0.008	0.0004	0.0003	0.0002	0.0002	0.001	0.001	0.001
Co59	0.012	0.011	0.006	0.004	0.008	0.005	0.007	0.081	0.004
<b>Cr283.563</b>	1.120	1.091	0.620	0.494	1.104	0.675	0.847	15.645	0.621
<b>Cu327.395</b>	1.652	0.465	0.358	0.413	0.837	0.789	0.869	2.528	1.020
Dy163	0.00002	0.0001	0.00003	0.00002	0.00003	0.00001	0.00003	0.0001	0.00004
Er167	0.00002	0.0002	0.000004	0.00001	0.00002	0.00001	0.00002	0.00003	0.00002
Eu151	0.00002	0.001	0.00001	0.00001	0.00002	0.00001	0.00001	0.00003	0.00001
<b>Fe238.204</b>	4.075	2.420	1.434	1.729	3.062	2.161	2.588	47.242	2.303
Gd157	0.0001	0.071	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001
Hf178	0.001	0.005	0.0003	0.0002	0.001	0.0005	0.0005	0.001	0.0004
Ho165	0.00001	0.0002	0.000005	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
<b>K766.491</b>	BD	0.236	BD	BD	0.038	0.010	BD	BD	BD

(continuing Table 5.3)

La139	0.0003	0.002	0.0002	0.0002	0.0002	0.0002	0.001	0.001	0.0004
Li7	0.001	0.002	0.002	0.004	0.002	0.001	0.002	0.004	0.001
Lu175	0.00001	0.00001	0.00001	0.000002	0.00001	0.00001	0.00001	0.00001	0.000004
<b>Mg279.553</b>	0.614	0.499	0.169	0.226	0.177	0.174	0.264	0.422	0.191
<b>Mn257.610</b>	0.063	0.066	0.048	0.041	0.082	0.059	0.069	1.023	0.094
Mo95	0.051	0.128	0.066	0.074	0.045	0.026	0.059	0.472	0.024
<b>Na588.995</b>	8.678	9.056	6.543	4.675	7.344	6.250	6.373	17.621	9.109
Nb93	0.002	0.063	0.003	0.018	0.002	0.004	0.004	0.010	0.001
Nd145	0.0002	0.014	0.001	0.0002	0.0001	0.0001	0.0004	0.001	0.0003
<b>Ni230.299</b>	2.240	2.079	0.558	0.949	1.705	1.042	1.620	18.858	0.747
<b>P213.618</b>	0.667	0.353	0.206	0.138	0.350	0.095	0.052	0.095	0.260
Pb208	0.079	0.036	0.026	0.041	0.066	0.023	0.027	0.139	0.083
Pr141	0.00004	0.645	0.0004	0.0001	0.00004	0.00003	0.0001	0.0001	0.0001
Rb85	0.001	0.007	0.001	0.001	0.001	0.001	0.001	0.001	0.001
<b>S180.669</b>	1970	211	189	1806	508	518	1102	1950	236
Sb121	0.018	20.681	0.059	0.045	0.020	0.019	0.019	0.028	0.017
<b>Si288.158</b>	4.472	2.862	1.587	2.087	1.353	3.172	4.774	2.634	3.344
Sm147	0.00004	0.0002	0.00003	0.00004	0.00004	0.00002	0.0001	0.0001	0.0001
<b>Sr407.771</b>	0.006	0.037	0.007	0.010	0.019	0.012	0.008	0.159	0.049
Th232	0.001	0.0002	0.0001	0.0001	0.001	0.0002	0.0002	0.0003	0.0002
<b>Ti334.941</b>	0.134	4.910	0.107	0.130	0.313	0.133	0.147	0.174	0.190
Tm169	0.00003	0.00003	0.001	0.00003	0.0002	0.0003	0.00003	0.0003	0.00003
U238	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
<b>V309.310</b>	5.410	BD	BD	0.707	0.002	0.0001	0.015	0.218	0.004
Yb172	0.00004	0.0001	0.00002	0.00001	0.00004	0.00002	0.00003	0.00004	0.00003
<b>Zn213.857</b>	1.077	1.609	0.918	0.894	1.467	0.936	0.842	8.911	0.999
Zr90	0.016	0.091	0.010	0.006	0.010	0.016	0.015	0.023	0.016

(continuing Table 5.3)

Analyte	J	A	W	X	C	B	Y	Z
Ag107	0.009	0.009	0.004	0.010	0.006	0.005	0.030	0.058
<b>Al396.152</b>	2.833	10.271	3.712	4.573	4.461	4.710	3.606	2.946
As75	0.547	0.312	0.144	0.142	0.236	0.166	0.108	0.190
<b>B249.772</b>	0.141	0.873	0.159	0.161	0.431	0.315	1.601	2.564
<b>Ba455.403</b>	24.712	48.396	0.015	25.004	5.718	0.032	0.030	0.127
Be9	0.001	0.011	0.001	0.001	0.003	0.003	0.001	0.001

(continuing Table 5.3)

<b>Ca396.847</b>	47.380	54.364	5.675	18.435	419.713	3.022	5.059	5.060
Cd111	0.014	0.015	0.004	0.003	0.009	0.008	0.001	0.002
Ce140	0.007	0.013	0.002	0.008	0.002	0.0003	0.001	0.001
Co59	0.029	0.009	0.010	0.053	0.047	0.020	0.069	0.701
<b>Cr283.563</b>	1.790	0.982	2.227	2.761	1.365	1.543	1.347	1.308
<b>Cu327.395</b>	1.564	0.846	2.339	4.330	2.296	1.216	0.593	0.716
Dy163	0.0003	0.001	0.0002	0.0004	0.0001	0.0001	0.0001	0.0001
Er167	0.0002	0.001	0.0001	0.0002	0.0001	0.00004	0.0004	0.0002
Eu151	0.003	0.006	0.0001	0.003	0.001	0.00004	0.00001	0.00004
<b>Fe238.204</b>	11.422	20.425	5.928	9.784	7.313	4.696	4.408	17.479
Gd157	0.001	0.001	0.0004	0.001	0.0003	0.0001	0.0001	0.0002
Hf178	0.001	0.002	0.0004	0.001	0.001	0.001	0.001	0.0004
Ho165	0.0001	0.001	0.00004	0.0001	0.00003	0.00003	0.0001	0.00004
<b>K766.491</b>	0.001	0.250	0.002	0.198	0.277	0.016	0.148	4.170
La139	0.003	0.004	0.001	0.004	0.001	0.0003	0.0003	0.0005
Li7	0.003	0.012	0.001	0.003	0.006	0.005	0.007	0.025
Lu175	0.0001	0.001	0.00003	0.0001	0.0001	0.0001	0.0002	0.0001
<b>Mg279.553</b>	0.278	0.437	0.188	0.657	0.740	0.215	0.572	0.790
<b>Mn257.610</b>	0.241	0.385	0.112	0.311	0.086	0.155	0.068	0.177
Mo95	0.177	0.076	0.191	0.101	0.241	0.068	0.101	0.122
<b>Na588.995</b>	4.676	2.848	5.637	13.443	28.696	11.300	32.048	63.579
Nb93	0.003	0.009	0.001	0.003	0.004	0.004	0.007	0.004
Nd145	0.002	0.003	0.001	0.003	0.001	0.0002	0.0002	0.001
<b>Ni230.299</b>	1.977	0.639	1.776	7.087	73.431	2.896	3.643	39.552
<b>P213.618</b>	1.048	1.882	0.390	0.216	2.642	0.732	1.251	0.098
Pb208	0.409	1.489	0.045	0.136	0.285	0.131	0.134	0.853
Pr141	0.001	0.001	0.0003	0.001	0.0002	0.0001	0.00005	0.0001
Rb85	0.001	0.002	0.001	0.003	0.003	0.001	0.002	0.020
<b>S180.669</b>	751	768	509	448	16663	1970	411	1241
Sb121	0.055	0.054	0.016	0.028	0.023	0.050	0.012	0.031
<b>Si288.158</b>	4.420	19.982	11.607	61.215	8.218	6.752	2.797	6.028
Sm147	0.0005	0.001	0.0003	0.001	0.0002	0.0001	0.00005	0.0001
<b>Sr407.771</b>	0.452	0.880	0.013	0.561	1.447	0.024	0.011	0.020
Th232	0.001	0.006	0.0002	0.001	0.001	0.001	0.0004	0.0003
<b>Ti334.941</b>	0.359	0.499	0.224	0.545	0.344	0.170	0.108	0.092
Tm169	0.0002	0.001	0.001	0.0001	0.003	0.004	0.0001	0.0001
U238	0.001	0.002	0.0002	0.0003	0.001	0.0004	0.001	0.0004
<b>V309.310</b>	BD	0.010	0.011	0.010	119.058	0.188	0.038	1.004

(continuing Table 5.3)

Yb172	0.0003	0.001	0.0001	0.0002	0.0002	0.0001	0.001	0.0004
<b>Zn213.857</b>	2.065	2.445	1.453	3.897	5.642	1.541	32.983	9.576
Zr90	0.023	0.030	0.017	0.019	0.021	0.008	0.018	0.014

### 5.3. Discussions

We have successfully analyzed 47 elements in the 26 crude oil samples. The analytes have potential applications in the oil industry as powerful indicators. Since the main objective of this study is to develop a working method for multi-elemental analysis in crude oils, I will introduce two examples about how to use the trace elements: 1) Identification of oil parent organic matter types and depositional environments of source rocks, and classification of oils by using Ni/V ratio, Ni + V, S (%), and Co/Ni; 2) The negative correlation between total transition metal content (Co, Cr, Cu, Mn, Ni, and V) and American Petroleum Institute (API) gravity.

Barwise (1990) reported that concentrations of trace metals in crude oils can be applied for classification of crude oils. Petroleum derived from marine organic matter is expected to have low Ni/V ratios ( $<0.5$ ), and high to moderate sulphur content, whereas petroleum derived from lacustrine and terrestrial organic matter is expected to have high Ni/V ratios (1–10), and low sulphur content. **Figure 5.2** indicates that sample C from Timan Pechora of Russia has the most marine organic matter input, whereas samples F from Jack County, K and L from Sterling County, and O from Irion County of Texas, U.S., and J from offshore Angola have the most non-marine organic matter input. Barwise (1990) also reported that since there is an abundant input of chlorophylls derived

from algae and bacteria to the organic matter of marine source rocks, and a good preservation of algae and bacteria derived chlorophylls under the more reducing conditions experienced by marine organic matter, high concentrations of metals, especially Ni and V, can be found in petroleum derived from marine organic matter.

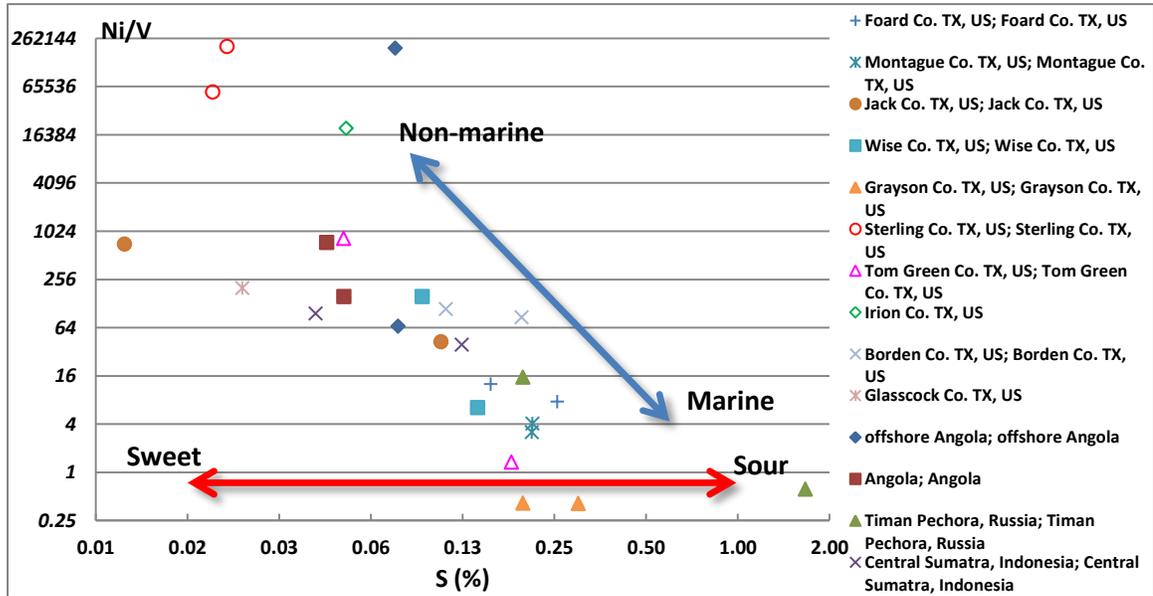


Figure 5.2. Ni/V ratio versus S content for organic matter types; Sample C from Timan Pechora of Russia has the most marine organic matter input, and highest S content; Samples F from Jack County, K and L from Sterling County, and O from Irion County of Texas, U.S., and J from offshore Angola have the most non-marine organic matter input, and relatively low S content; Note: this is a log-scale plot

Based on the systematic classification of crude oils made by Filby (1994) and Barwise (1990), we classified the 26 natural crude oil samples. The results are listed in **Table 5.4.**

Table 5.4. Parent organic matter type, depositional environment and oil type of the 26 natural crude oil samples based on the measured concentrations of V, Ni and S; P/B: phytoplankton/bacteria; TP: terrestrial plants; MNS: marine non-siliciclastics; MS: marine siliciclastics; L: lacustrine; NM: non-marine

	Foard Co. TX	Foard Co. TX	Montague Co. TX	Montague Co. TX	Jack Co. TX	Jack Co. TX	Wise Co. TX	Wise Co. TX	Grayson Co. TX
S (%)	0.15±0.005	0.26±0.008	0.21±0.006	0.21±0.006	0.01±0.003	0.11±0.003	0.14±0.004	0.09±0.003	0.30±0.009
Ni (ppm)	6.023±0.084	11.347±0.158	2.724±0.038	1.563±0.022	1.693±0.024	5.211±0.072	1.679±0.023	5.582±0.078	7.444±0.103
V (ppm)	0.477±0.006	1.48±0.017	0.671±0.008	0.491±0.006	0.002±0.00003	0.122±0.001	0.261±0.003	0.036±0.0004	18.254±0.214
Ni+V (ppm)	6.500±0.090	12.827±0.175	3.396±0.046	2.055±0.028	1.696±0.024	5.333±0.073	1.940±0.026	5.617±0.078	25.697±0.317
Ni/V	3.549±0.324	3.521±0.197	2.127±0.104	18.982±0.082	1362±18.136	12.812±1.098	6.533±0.165	28.944±4.017	0.092±0.010
Parent organic matter type	P/B	/	P/BorTP	TP	TP	P/BorTP	TP	P/BorTP	/
Depositional environment	L	/	LorNM	NM	NM	LorNM	NM	LorNM	/
Oil class	C	/	CorDorE	DorE	DorE	CorDorE	DorE	CorDorE	/

(continuing Table 5.4)

	Grayson Co. TX	Sterling Co. TX	Sterling Co. TX	Tom Green Co. TX	Tom Green Co. TX	Irion Co. TX	Borden Co. TX	Borden Co. TX	Glasscock Co. TX
S (%)	0.20±0.006	0.02±0.001	0.02±0.001	0.18±0.005	0.05±0.001	0.05±0.002	0.11±0.003	0.20±0.006	0.02±0.001
Ni (ppm)	2.240±0.031	2.079±0.029	0.558±0.008	0.949±0.013	1.705±0.024	1.042±0.014	1.620±0.023	18.858±0.262	0.747±0.010
V (ppm)	5.41±0.064	BD	BD	0.707±0.008	0.002±0.00002	0.0001±0.000001	0.015±0.0002	0.218±0.003	0.004±0.00004
Ni+V (ppm)	7.649±0.095	>2.050	>0.550	1.657±0.021	1.707±0.024	1.043±0.014	1.635±0.023	19.076±0.265	0.751±0.010
Ni/V	1.032±0.011	>20500	>5500	2.941±0.034	279±21.410	9490±504.346	496±2.804	10.275±2.216	405±5.111
Parent organic matter type	/	TP	TP	P/BorTP	TP	TP	TP	/	TP
Depositional environment	/	NM	NM	LorNM	NM	NM	NM	/	NM
Oil class	/	DorE	DorE	CorDorE	DorE	DorE	DorE	/	DorE

(continuing Table 5.4)

	Offshore Angola	Offshore Angola	Angola	Angola	Timan Pechora, Russia	Timan Pechora, Russia	Central Sumatra, Indonesia	Central Sumatra, Indonesia
S (%)	0.08±0.0 02	0.08±0.0 02	0.05±0.0 01	0.04±0.0 01	1.67±0.04 9	0.2±0.00 6	0.04±0.0 01	0.12±0.0 04
Ni (ppm)	1.977±0. 027	0.639±0. 009	1.776±0. 025	7.087±0. 099	73.431±1. 021	2.896±0. 04	3.643±0. 051	39.552±0 .550
V (ppm)	BD	0.01±0.0 001	0.011±0. 0001	0.01±0.0 001	119.058±1 .398	0.188±0. 002	0.038±0. 0004	1.004±0. 012
Ni+V (ppm)	>1.950	0.649±0. 009	1.787±0. 025	7.097±0. 099	192.489±2 .419	3.084±0. 042	3.681±0. 051	40.556±0 .562
Ni/V	>19500	63.9±1.7 06	1714±4.0 21	74.8±18. 955	0.617±0.0 16	15.404±0 .396	95.868±2 .467	39.394±1 .011
Parent organic matter type	TP	TP	TP	P/BorTP	P/B	TP	TP	/
Depositi onal environ ment	NM	NM	NM	LorNM	MNS	NM	NM	/
Oil class	DorE	DorE	DorE	CorDor E	A	DorE	DorE	/

Udo et al. (1992) reported that Co/Ni ratios greater than 0.1 infer crude oil source rocks that have more marine source input. The Co/Ni ratios of our crude oil samples range from 0.001-0.019 with an average value of 0.006, inferring a dominant input of non-marine organic matter. This agrees with our interpretation (**Table 5.4**) except for sample C.

Akinlua et al. (2007) reported that V, Ni, and total transition metal (TTM) content decreases as terrestrial input increases, because they are inversely correlated with Pr/Ph ratio. In our study, sample C from Timan Pechora of Russia has the highest abundances of V, Ni, and TTM, so it has the lowest terrestrial organic matter input. This also agrees with our interpretation (**Table 5.4**).

Sample H from Foard County can be clearly classified into Family C, because its  $(Ni + V)$  is less than 10 and greater than 5, and Ni/V ratio falls into 2-10 ppm (wt./wt.), based on Filby's classification. Sample D from Montague County, G from Jack County, Q from Wise County, M from Tom Green County, and X from Angola can only be classified into Family C, or D, or E, because both the  $(Ni + V)$  and Ni/V of sample G, Q, and X are greater than 5, and both the  $(Ni + V)$  and Ni/V of sample D and M are smaller than 5. It is hard to classify sample I from Foard, R and S from Grayson, U from Borden, and Z from Central Sumatra of Indonesia, because the  $(Ni + V)$  of sample I, R, U, and Z, and the Ni/V of sample S do not fall into any region for classification. Therefore, although trace metals can be used as powerful indicators for parent organic matter type and depositional environment of source rock, additional indicators are needed for more specific classification.

Lewan (1984) reported that low Ni/V ratio is associated with anoxic depositional environment, and reported that  $V/(V + Ni)$  ratio is inversely correlated with even predominance of Pr/Ph ratio and n-alkanes, whereas positively correlated with Ph/nC18 ratio. This indicates input of marine organic matter. This agrees with what Barwise (1990) reported. **Table 5.4** indicates that sample F from Jack County, K and L from Sterling County, N from Tom Green County, O from Irion County, T from Borden County, V from Glasscock County of Texas, U.S., J from offshore Angola, and W from Angola are associated with strong oxic depositional environment, because they have much higher Ni/V ratios than the other samples. Samples R and S from Grayson County of Texas, U.S., and C from Timan Pechora of Russia have the lowest Ni/V ratios,

inferring the strongest anoxic depositional environment. Lewan (1984) also reported that concentrations of V and Ni greater than 100 ppm are observed in bitumens with respect to kerogens of Type I and II, and the concentrations of V and Ni less than 100 ppm are contained in bitumens relevant to Type III kerogens. **Table 5.4** indicates that only sample C from Timan Pechora of Russia has concentrations of V and Ni greater than 100 ppm, which means that only sample C is associated with kerogens of Type I and II, and this further indicates marine depositional environment of sample C. The other samples are associated with Type III kerogens, inferring terrestrial origin. Thus, our interpretation shows a good agreement with Lewan's work.

Oluwole et al. (1993) reported that the total transition metal content is negatively correlated with American Petroleum Institute (API) gravity, and the API gravity is also negatively correlated with each of Cr, Cu, Mn, Ni, Se, and V. We checked the data of Co, and found that it is also negatively correlated with API gravity. Barwise (1990) also reported that only low or moderate API gravity crude oils can be found with high content of transition metals. **Figure 5.3** shows that samples C from Timan Pechora of Russia, Z from Central Sumatra of Indonesia, and U from Borden County in Texas of U.S., have the highest total content of Co, Cr, Cu, Mn, Ni, and V of 196.3, 43.46, and 38.35 ppm (wt./wt.), and they are very heavy black crude oils with high viscosity. The total content of Co, Cr, Cu, Mn, Ni, and V of samples A and J from offshore Angola, and F from Jack County, K and L from Sterling County, and O from Irion County in Texas of U.S., ranges from 1.59-5.6 ppm (wt./wt.) with an average value of 3.641 ppm (wt./wt.). As a matter of

fact, these samples are very light and transparent brown crude oils with low viscosity. This agrees with Oluwole et al. (1993) and Barwise (1990) very well.

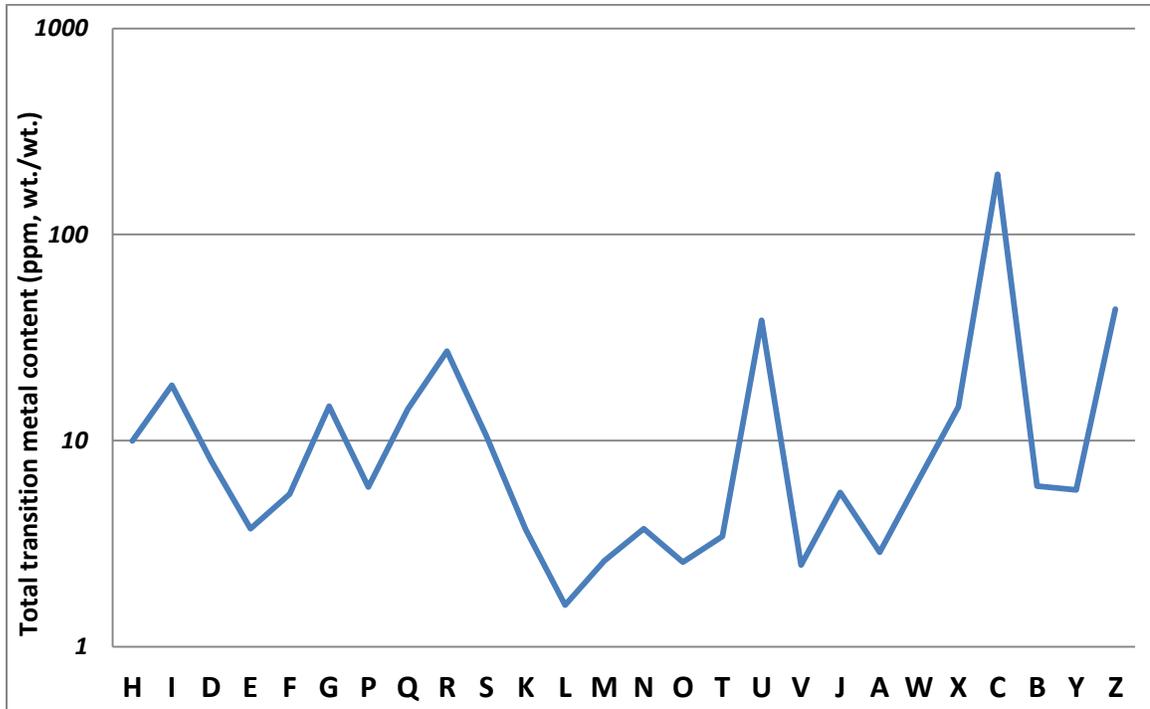


Figure 5.3. Total transition metal content (Co, Cr, Cu, Mn, Ni, and V) of the 26 crude oil samples; Information of samples H-Z refers to Table 5.2; Note: this is a log-scale plot

## Conclusions

There might be significant loss of analytes during combustion sample preparation procedure, which might be caused by volatilization of volatile species of the target elements.

The developed working method with acid digestion can be used to do multi-elemental analysis in crude oils.

Accurate concentrations of 46 elements together with V in NIST 8505 have been constrained, among them, Al, Ba, Co, Cu, Mg, Mn, Ni, and Sr have been tested by both ICP-OES/ICP-MS which showed a good agreement within analytical error range.

Trace elements can be used as powerful indicators in classification of crude oils, identification of oil organic matter types, aspects of depositional environment of source rocks, and oil API gravity.

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