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COMPARISON OF CLOSED-PRESSURIZED AND OPEN-REFLUXED VESSEL DIGESTION SYSTEMS FOR TRACE ELEMENTS IN THE RESIDUAL FUEL OIL REFERENCE MATERIAL (SRM 1634c)

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ABSTRACT. Samples of residual fuel oil reference material (SRM 1634c) were mineralized in closed digestion vessels from Milestone Laboratory Systems (MLS) or from PAAR (HPA) or in open-refluxed microwave digestion flasks from Prolabo. The three digestion systems were evaluated in terms of accuracy and precision, reagents and time saving, total organic carbon content, and method determination limits for the determination of trace elements (Be, Mg, Al, Ca, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Te, Ba, Hg, Tl, Pb, Bi, U) by inductively coupled plasma-mass spectrometry. The total organic carbon concentrations were 1160 (MLS), 240 (HPA), and < 10 (Prolabo) mg C kg^{-1}. Concentrations of V, Ni, and As in the digests of the HPA and the MLS systems were in acceptable agreement with each other and with the certified values for these elements. The values for Co when using the HPA and the MLS systems were lower than the certified Co value (~80%). Higher values for Se are probably due to interference by ^{82}Kr. The digests of the HPA were prone to contamination by Fe and Al from the digestion chamber. The Prolabo system generally resulted in a substantial reduction in the concentration of elements, probably due to volatilization losses. It was also prone to sulfur-based interference. For the majority of the elements the relative standard deviations (RSD, n = 5) were less than 5% for HPA and MLS but were higher than 10% for Prolabo.

INTRODUCTION

Crude oil and a variety of its products are used around the world to provide energy. Among the various products, residual fuel oil is the heavier and highly viscous fraction used in electric power generation, industrial steam generation, process heating, and steamship operation [1]. During its combustion, appreciable amounts of trace elements are emitted that can be harmful to the environment by affecting life processes in undesirable ways. Regulations that limit emission levels of toxic elements from fuel oil-fired plants have already been in place in some countries [2-4]. As a result of such concerns, the residual fuel oils are required to meet air-pollution regulations in addition to other quality standards. In response to such demands, a growing interest is evident whereby methods that permit the accurate analysis of fuel oil used in oil fired-power plants [2-4] so that environmental impact can be evaluated.

In many instances trace elements occur at very low concentrations in crude oil samples. In order to measure such low levels, one line of attack is to process a larger mass of sample to obtain a final solution concentration that is sufficiently above the detection limit of the instrumental technique [5]. However, the advent of instruments with a capability to detect multi-elements at increasingly lower concentrations (*e.g.*, ICP-MS) eased significantly the requirements on the sample size. The fact that only liquid solutions are compatible with the

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standard ICP-MS instrumentation requires processing of samples prior to analysis. On the other hand, the demand to prepare large numbers of samples in less time and with greater efficiency is fostered by multi-elemental instruments [6].

Common methods employed for the preparation of petroleum samples include dry ashing or wet-oxidation in open vessels [7-10], dilution with organic solvents [11-13], and formation of oil-in-water micro-emulsions [5,7,14-18]. Loss of the more volatile elements such as Hg, As, Se, Sb, Ni, and V becomes a serious problem with dry ashing procedures [4,5]. The addition of benzenesulfonic acid [19], *p*-xylenesulfonic acid [20], or sulphanilic acid [21] effectively decreases volatilization losses of specific analytes. Generally, lengthy time requirements and poor accuracy and precision [6] often make these procedures undesirable.

Dilution of petroleum samples with an organic solvent (*e.g.* xylene) and subsequent introduction into the ICPs substantially degrades the performance of ICPs in terms of plasma stability and detection limits relative to aqueous solutions. In addition, these methods require the use of expensive and readily unavailable organometallic standards [22] and are prone to increase interference from carbon-based polyatomic ions derived from the solvent [23].

The application of oil-in-water microemulsions into plasmas minimizes the use of organic solvents in the sample preparation, allows the use of aqueous standards, and eliminates the need to devise elaborate mechanisms for removing solvent vapors from the aerosol stream [15]. However, the high limits of detection [2,5] seriously prevent extensive application of oil-in-water microemulsions.

The most desirable features of procedures used for the preparation of petroleum samples include rapid processing with a minimal quantity of reagents, improved accuracy and precision as a result of decreased risk of contamination and reduced loss of the more volatile analytes, enhanced oxidation potential of digestion reagents at temperatures higher than the boiling point of the reagents, and possibilities to use aqueous standards.

Of the available techniques, systems that use electrical energy for heating in closed-vessels and systems that utilize microwave energy appear the most promising approaches to abating the problems associated with the preparation of petroleum samples. In fact, presently microwave digestion systems have replaced many open-vessel decomposition procedures because of the remarkable advantages they offer. Open-vessel microwave digestion systems with reflux facilities that are developed in attempts to easing the problems with sample size allow digestions of large masses of petroleum samples with a focused-microwave energy [5] while retaining volatile elements by a reflux mechanism. Despite the compelling need for methods that permit the determination of a wide range of trace elements in the residual fuel oil at lower concentrations, attempts were not made in previous studies to develop and systematically evaluate the performance of the most promising digestion systems in order to provide recommendations.

Being the heaviest distillate fraction of petroleum, the residual fuel oil poses a special difficulty to digest. The achievable temperatures with the available microwave equipment may not allow complete destruction of organic matter in this sample. The presence of undigested organic residues may affect the performance of spectrometric techniques based on solution nebulization [24]. Although such problems can be overcome by internal standardization and the standard addition methods, time and money saving and convenience demand the use of external calibration method. The high pressure asher [25] appears highly promising because it provides temperatures as high as 320 °C and pressures as high as 130 bars to ensure complete destruction of organic matter in closed digestion vessels.

In the present study, three commercially available digestion systems that employ microwave or electrical energy as source of heat were used to decompose the residual fuel oil

(NIST SRM 1634c). In the digests, trace elements were determined by ICP-MS. The digestion procedures were evaluated in terms of accuracy, precision, completeness of organic matter decomposition, speed of digestion, limits of determination, and time and reagent savings.

EXPERIMENTAL

Digestion systems

Closed-pressurized microwave digestion system. The Milestone Microwave Digestion System (MLS 1200 MEGA, Leutkirch, Germany) operating at a microwave frequency of 2450 MHz was used for digesting the residual fuel oil reference material SRM 1634c "Trace elements in Fuel Oil" (National Institute of Standards and Technology, Gaithersburg, USA). The instrument is equipped with a rotor (type MDR-1000/6/100/110) suitable for simultaneously digesting six samples, a fume extraction module, a capping station, and a control panel with alphanumeric display. The maximal power of the microwave generating magnetron is 1200 W with 1000 W delivered inside the working chamber. Microwave emission is "unpulsed" in the 250-W and 1000-W modes, but it is pulsed with 1000 W delivered for adjustable fractions of a cycle whenever any other power between 250 and 1000 W is required.

Open-refluxed microwave digestion system. Model Microdigest A 301 (Prolabo, Paris, France) equipped with a programmer, a 3-way reagent filling pump, a turn table capable of holding 16 digestion flasks, a single digestion-well, and a robotic arm for loading and unloading the digestion well with flasks was used. The microwave generating magnetron operates at 2450 MHz and delivers 200 W continuously. The digestion mixture is irradiated with a microwave power that can be programmed to vary in steps of 5% in the range 10 to 99% of the full power. The digestion step, the digestion reagent, the reagent volume, the power, and the time were specified in programming the mineralization procedure.

The high pressure asher. The high pressure asher (PAAR, Graz, Austria) that decomposes samples in closed-pressurized vessels under high temperature and pressure was used for the digestion of SRM 1634c. The HPA consists of an autoclave that should be filled with high purity argon or nitrogen gas, a stainless steel heating block (with 7-borings), quartz decomposition vessels, a temperature controller (model HPA-TC), and a personal computer. The PC transmits the temperature program to the HPA-TC via serial interface (RS 232 C) and displays the actual temperature and pressure profile. The autoclave is heated electrically in the range 30-320 °C. A minimum pressure of 100 bars should be supplied by the gas cylinder for the operation of the HPA system. With increasing temperature the autoclave pressure can reach up to 130 bars and a higher pressure is released through the safety valves.

Inductively coupled plasma-mass spectrometer

The Hewlett Packard Model HP 4500 inductively coupled plasma-mass spectrometer (Yokogawa Analytical Systems, Tokyo, Japan) fitted with a Babington nebulizer was used for the determination of total element concentrations in the NIST SRM 1634c. The operating conditions (Table 1) were optimized using a tuning solution of Li, Y, Ce, and Tl. The doubly charged and oxide levels were checked with Ce.

Reagents and solutions

Milli-Q$^+$ water that was purified to 18.2 MΩ.cm resistivity was used for preparing solutions and rinsing containers. All commercial grade chemicals were used without further purification unless indicated otherwise. Concentrated nitric acid, HNO_3, (Merck 100456, 65%) purified in a *duoPUR* subboiling unit (Milestone Laboratory System, Leutkirch, Germany), a *suprapur* grade hydrogen peroxide, H_2O_2, (Merck 107298, 30%), and sulfuric acid, H_2SO_4 (Merck 714, 96%) were used as reagents for digestion of the residual fuel oil and preparation of blanks.

A stock solution containing multi-element standards was prepared by mixing the following solutions in 10-mL disposable test tube and diluting to 10 mL with Milli-Q$^+$ water: 1.00 mL of the ICP Multi-Element Standard VI (Merck, Darmstadt, Germany, 110580), 1.00 mL of Hg-Sn-Sb standard (10 mg element/L, a mixed intermediate standard prepared from Merck, 1000 mg element/L), 1.00 mL of conc. HNO_3, 90.0 µL of Ba (1000 mg Ba/L, Merck 19774), 90.0 µL of Ni (1000 mg Ni/L, Merck 9989), and 90.0 µL of V (1000 mg V/L, Baker 019146). Calibration standards were prepared by spiking digested and diluted solutions of reagents with the stock solution. A mixture of conc. HNO_3 (5.0 mL), and 30% H_2O_2 (2.0 mL) was digested with the HPA and MLS systems and was diluted to 40 mL after addition of the internal standards (160 µL each of Sc and In, 10 µg elementL). With the Prolabo system conc. HNO_3 (8.0 mL), 30% H_2O_2 (2.0 mL) and conc. H_2SO_4 (7.0 mL) were digested and subsequently evaporated to a volume of ~3.0 mL. To this residue, solutions of Sc and In (160 µl, 10 µg element/L) were added and the resulting mixture was diluted to 40 mL. Each of the 40-mL reagent solutions obtained with the three digestion systems was divided into four test tubes (10-mL portions to the first, second, and third test tubes and the remainder solution into the fourth test tube). The contents of the four test tubes were spiked with 0.0, 10.0, 50.0, or 100 µL of the stock solution to give 0.0, 1.0, 5.0, or 10 µg element/L of Mg, Al, Cr, Mn, Co, Cu, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Te, Hg, Tl, Pb, Bi, and U; 0, 10, 50, or 100 µg element/L of Be, V, Fe, Ni, Zn, As, Se, and Ba; and 0, 100, 500, or 1000 µg Ca/L.

Table 1. Operating conditions for the Hewlett Packard HP 4500 ICP-MS.

Nebulization		
Nebulizer	Babington	
Spray chamber	Peltier-cooled double pass Scott type (2°C)	
Nebulizer gas	1.07 L/min	
Back pressure	650 kPa	
Inductively coupled plasma mass spectrometer		
Plasma	Rf power, forward	1.30 kW
	Rf power, reflected	< 2 W
Argon gas flow rate	Cooling	15 L/min
	Auxiliary	1.00 L/min
Vacuum	Interface	12 kPa
	Analyzer	2.0×10^{-4} kPa
Ion sampling cones	Sampler	Platinum, orifice, 1.00-mm dia.
	Skimmer	Nickel, orifice, 0.4-mm dia.
Measuring parameters	Uptake	45 s at 2 mL/min
	Sampling depth	4.4 mm
	Stabilization	30 s at 0.4 mL/min
	Integration time	varied with element
	Wash time	60 s at 2 mL/min
	Replicates	3

Analytical Procedure

Mineralization of the residual fuel oil (SRM 1634c) in a closed-pressurized microwave digestion system. The residual fuel oil SRM 1634c was microwave digested according to a previously optimized procedure [26]. An aliquot (~250 mg) of the oil placed in each of five digestion vessels was treated with conc. HNO_3 (5.0 mL) and 30% H_2O_2 (2.0 mL). Digestion was carried out applying the nine-stage digestion program (Table 2). After the program had been completed, the vessels were brought into a well-ventilated hood; the digests were transferred into graduated sample tubes, and diluted to 40 mL with Milli-Q® water after addition of 160 µL of an internal standard solution (10 mg Sc/L and 10 mg In/L).

Table 2. Optimized heating programs for the digestion of SRM 1634c (~250 mg) with an HPA, MLS, and the Prolabo digestion systems.

Parameter for digestion system		Digestion step								
		1	2	3	4	5	6	7	8	9
Power (W)	MLS	300	0	450	0	450	0	300	0	400
	HPA	-	-	-	-	-	-	-	-	-
	Prolabo	60	80	100	120	140	120	198[a]	-	-
Temp. (°C)	MLS[b]									
	HPA	60	120	280-300	-	-	-	-	-	-
	Prolabo[c]									
Time (min)	MLS	2	0.5	10	0.5	10	0.5	9.5	0.5	3
	HPA	60	60	100	-	-	-	-	-	-
	Prolabo	10	10	5	10	5	5	65[a]	-	-

[a]Evaporation step; [b]temperature varied from room temperature to 230 °C [26]; [c]temperature limited to boiling point of digestion mixture.

Digestion of the residual fuel oil (NIST SRM 1634c) in a high pressure asher. Into a labeled, clean, tared, 50-mL quartz decomposition vessel the fuel oil (~250 mg) was transferred with the aid of an acid-washed, rinsed, and dry glass rod. The loaded vessel was weighed to 0.1 mg. The fuel oil in the vessel was mixed with 5.0 mL of HNO_3 (65%) and 2.0 mL of H_2O_2 (30%). The mouth of the vessel was sealed with a strip of PTFE (~2.5 x 2.5 cm). The PTFE-seal strip was punctured with the nozzle of a clean glass dropper. A quartz lid was put on the PTFE-strip and the neck of the vessels was wrapped together with the lid with a PTFE-strip (~10 cm long) and the upper tip of the strip was bent in-wards in such a way that it rests completely on the lid.

Seven such loaded and sealed decomposition vessels were placed into the borings of the heating block. The heating block loaded with the vessels was placed into the heating chamber. The lid was placed on the heating chamber and the half ring retainers were placed from front and back of the lid and were screwed tightly with an Allen wrench. After filling the heating chamber with high purity argon (99.999%, Messer Griesheim, Graz, Austria) the heating program (Table 2) was started. After the digestion program had been completed, the heating block was allowed to cool to 40-50 °C. The autoclave was then opened and the quartz vessels were removed from the heating block. The digests in the vessels were transferred into sample tubes. The vessels were rinsed three times with about 5-mL portions of Milli-Q® water and the rinsings combined with the digests in the tubes. After addition of 160 µL of the internal standard solution (Sc and In, 10 µg element/L) the digests were diluted to 40 mL with Milli-Q® water.

Digestion of the residual fuel oil (SRM 1634c) in an open-focused microwave unit. Aliquot (~250 mg) of the NIST SRM 1634c were weighed to 0.1 mg into each of five digestion flasks The flasks containing the fuel oil and an empty digestion flask (for the blank) all fitted with reflux condenser, were placed into the numbered wells of the Microdigest A 301 carousel After the program (Table 2) had been started, the robotic arm automatically transferred on flask from the carousel into the digestion well. The digestion reagents added automatically i the order given in Table 2 and the irradiation of the digestion mixture was started. At the en of the digestion program the robot arm was switched to the evaporation position to remov the excess acid. After the end of evaporation step, the flask was returned to the turntable an the next digestion flask was placed into the digestion well. The clear digests were transferre into plastic sample tubes, after sufficient cooling had been achieved within 10 min, an diluted to 40 mL with Milli-Q® water after addition of 160 µL of the internal standard solutio (Sc and In, 10 µg element/L).

Determination of total organic carbon concentration (TOC) in the digests. In addition t visual evaluation of the completeness of decomposition, the total organic carbo concentration was determined at the Institute for Analytical Chemistry, Micro- an Radiochemistry (Technical University of Graz, Graz, Austria).

RESULTS AND DISCUSSION

Digestion of the residual fuel oil

The microwave program optimized for the residual fuel oil SRM 1634b [26] was directly use for mineralizing the SRM 1634c. When visually inspected the diluted digests of the ML system were yellowish apparently indicating incomplete decomposition of the hydrocarbo matrix, but contained no particulate matter. A typical program recommended by th manufacturer of HPA for mineralizing biological and environmental samples was used fo digesting SRM 1634c with the HPA system (Table 2). The digests with the high pressur asher obtained using the heating program that lasted 220 min were colorless showin complete destruction of the hydrocarbon matrix. The high pressure asher allows digestions a temperatures up to 320 °C and pressures up to 130 bars. Such high temperature condition could not be used with the MLS system primarily because the TFM (Tetrafluormethaxil Regulated Trademark of the Hoechst Company) digestion vessels begin to soften at ~250°C Also, the digestion vessels are vented at pressures ~50 bars probably ejecting portions of th analytes in the form of aerosols.

The open-focused digestion system of Prolabo delivers 200 W continuously. Sinc mineralization with this digestion equipment is performed in an open system the maximu temperature achievable is limited by the boiling point of the digestion mixture. Because th microwaves are directly focused on the digestion mixture [24], digestion times are remarkabl reduced compared to hot-plate procedures. During the optimization step the digestio procedure (Table 2) was begun with a low microwave power (30%) to avoid initiation o vigorous reactions and possible loss of analytes. Attempts to digest ~250 mg of the fuel o with 25 mL of HNO_3 (65%) and 7.0 mL of H_2O_2 (30%) applying 30-75% power for 62 mi resulted in carbonization. Digestions for 55 min (Power 30-60%) with 10.0 mL of HNO_3, 5. mL of H_2SO_4, and 3.0 mL of H_2O_2 resulted in brownish solution. These results showed th insufficiency of a mixture of HNO_3 and H_2O_2 for the decomposition of the fuel oil. Therefor

in the subsequent experiments a mixture of HNO_3-H_2O_2-H_2SO_4 was used. Mixtures of HNO_3 (8 mL), H_2SO_4 (5 mL), and H_2O_2 (2 mL) did not give a colorless digest after a 55-min digestion period. An optimal procedure that allowed the digestion of the fuel oil (~250 mg) required 8.0 mL of HNO_3 (65%), 7.0 mL of H_2SO_4 (96%) and 2.0 mL H_2O_2 (30%). The digestion program lasted 45 min followed by a mandatory evaporation step of 65-min (Table 2). When visually inspected, the digests (~3 mL) were clear and colorless. The 125-mL digestion flasks are fitted with air-cooled reflux condensers to efficiently condense the escaping acid vapors. Despite such provisions, the acid fumes reach the injection head and condense there as noted by Krachler *et al.* [27].

The digestion and cooling times and reagents consumed are summarized for each of the digestion systems (Table 3). The MLS and the HPA systems consumed the same amounts of HNO_3 and H_2O_2, whereas the acid volume needed for digestion by the Prolabo system was more than double the amount needed by the former two. The time required for mineralizing SRM 1634c (~250 mg) varied in the order (System/No. of samples: MLS/6, PAAR/7, Prolabo/6) 36.5, 220, 270 min and for cooling 40, 60, 60 min. The Prolabo system is equipped with only one digestion well as a result, a total digestion and evaporation time of 660 min was required for mineralizing the fuel oil in each of five digestion flasks and a reagent blank.

Table 3. Comparison of reagent consumption and digestion time required by the HPA, the MLS, and the Prolabo systems for mineralizing ~250 mg of the residual fuel oil (SRM 1634c).

Variable	Digestion system		
	HPA	MLS	Prolabo
HNO_3, mL	5.0	5.0	8.0
H_2SO_4, mL	-	-	7.0
H_2O_2, mL	2.0	2.0	2.0
Time, min	220	37	660
No of vessels	7	6	6

Concentration of total organic carbon (TOC) in the digests

The concentration of total organic carbon is a measure of the degree of destruction of organic matter. The total organic carbon concentration (n = 5) in the digests of the MLS system was (1160 ± 150 mg C/kg), in the HPA system (240 ± 50 mg C/kg), and in the Prolabo system (< 10 mg C/kg). According to Knapp *et al.* [24] a temperature of at least 300 °C is required to completely decompose organic matrix. Since this target temperature cannot be supplied by the MLS system, the resulting yellowish digests exhibited relatively higher concentrations of TOC. These results generally showed the high digesting power of the prolabo system with a mixture of HNO_3-H_2O_2-H_2SO_4.

Determination of trace elements in the digests of the SRM 1634c

The Hewlett Packard inductively coupled plasma-mass spectrometer (HP 4500) was used for the determination of trace elements in the digests of the HPA, MLS, and the Prolabo systems. The operating conditions for the HP 4500 are summarized in Table 1. Twenty eight trace elements (Be, Mg, Al, Ca, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Te, Ba, Hg, Tl, Pb, Bi, and U) were determined in the digests employing standard addition

calibration. Preparation of matrix matched standards would be impractical in presence of high TOC in the digests while none in the blank. Thus, the application of standard addition calibration appears justifiable. Support for this conviction comes from the study of the variation in the raw counts of the two internal standards (^{45}Sc and ^{115}In, 40 µg element/L), added to calibration standards and the digests obtained using the three digestion systems. The digests of the HPA system caused little or no signal fluctuation, whereas, appreciable differences between standards and the fuel oil digests were observed for the MLS and the Prolabo systems. It seemed logical to infer that the organic residue in the oil digests of the HPA system was not high enough to influence the count rates of the internal standards and that the difference between the blanks and the oil digests was minimal. To correct for signal fluctuation, scandium (^{45}Sc) was used for elements with mass numbers ≤ 82 and ^{115}In for elements with mass numbers ≥ 85 in solutions obtained using the three digestion systems.

In view of the existence of C and/or Si based interferences in environmental samples, the choice of ^{45}Sc as an internal standard might become of concern. To check the validity of choosing ^{45}Sc, the trends in the raw counts of the internal standards (^{45}Sc and ^{115}In) were examined. Interference on Sc (*e.g.*, $^{28}Si^{16}O^{1}H$, $^{29}Si^{16}O$ or $^{12}C^{16}O^{16}O^{1}H$) should increase the raw count rate of ^{45}Sc and should have no similar effect on that of ^{115}In. However, such effects were not apparent from the raw counts of the internal standards. In addition, molecular interference on ^{45}Sc depends a lot on the running conditions of the ICP-MS. High oxide ratios certainly cause such interference. Normally our system is well tuned, as a result of which the occurrence of interferences of the above nature is less likely. Furthermore, the observed good agreement of experimental results with the certified data indicates that Sc was a good choice.

Selection of suitable isotopes for ICP-MS

Wherever possible, isotopes free from polyatomic interference were chosen for signal evaluation. Signal enhancement caused by background molecular ions (digestion reagents) and polyatomic ions formed from matrix components are compared for selected elements (Figures 1a and 1b). The three digestion systems gave similar concentrations for the pair of isotopes of Mg, Ni, Sr, and Ba. Such similarity in signals could be due to absence of species causing signal enhancement or presence of interference to the same degree on both isotopes. The vanadium isotope ^{50}V can be interfered by $^{36}Ar^{14}N^{+}$ from nitric acid and the argon gas. Furthermore, the low natural abundance (0.25%) of ^{50}V makes it unsuitable for quantitative evaluations. To avoid chloride-based interference, the selenium isotope (^{82}Se) with a natural abundance of 8.73% was used for the determination of selenium. The major polyatomic ions from digestion acids and matrix components that could potentially interfere with the determination of the following elements are described below.

Ca. The isotope ^{44}Ca is prone to interference from $^{12}C^{16}O_2^{+}$. Consequently, the HPA and the MLS digestion systems gave higher concentrations for ^{44}Ca than ^{43}Ca (Figure 1a). Therefore, the concentration of Ca was evaluated using ^{43}Ca, an isotope with only 0.135% relative natural abundance.

Cr. The concentration of ^{52}Cr was higher than ^{53}Cr in the digests of the three systems (Figure 1a). The ^{52}Cr isotope suffers from polyatomic ions such as $^{40}Ar^{12}C^{+}$, $^{38}Ar^{14}N^{+}$, $^{36}Ar^{16}O^{+}$, $^{35}Cl^{16}O^{1}H^{+}$, and $^{36}S^{16}O^{+}$. The digests of MLS system contain more dissolved carbon compared to the HPA and the Prolabo systems. As a result, the MLS system gave higher values for ^{52}Cr perhaps due to enhancement by $^{40}Ar^{12}C^{+}$. Therefore, the minor isotope of chromium (^{53}Cr,

9.5%) is recommendable for determinations of chromium in the MLS digests of SRM 1634c and similar matrices. The concentrations of TOC in the digests of the HPA and MLS systems were relatively higher than in the Prolabo digests and hence carbon-based interference ($^{40}Ar^{12}C^{+}$) should be more on ^{52}Cr. The Prolabo system that is relatively free from such interference (due to more complete decomposition of hydrocarbons), though minor could suffer from $^{34}S^{18}O^{+}$. The discussions made so far give sufficient ground to reject the more abundant isotope (^{52}Cr, 83.79%) for quantification of total chromium in the fuel oil.

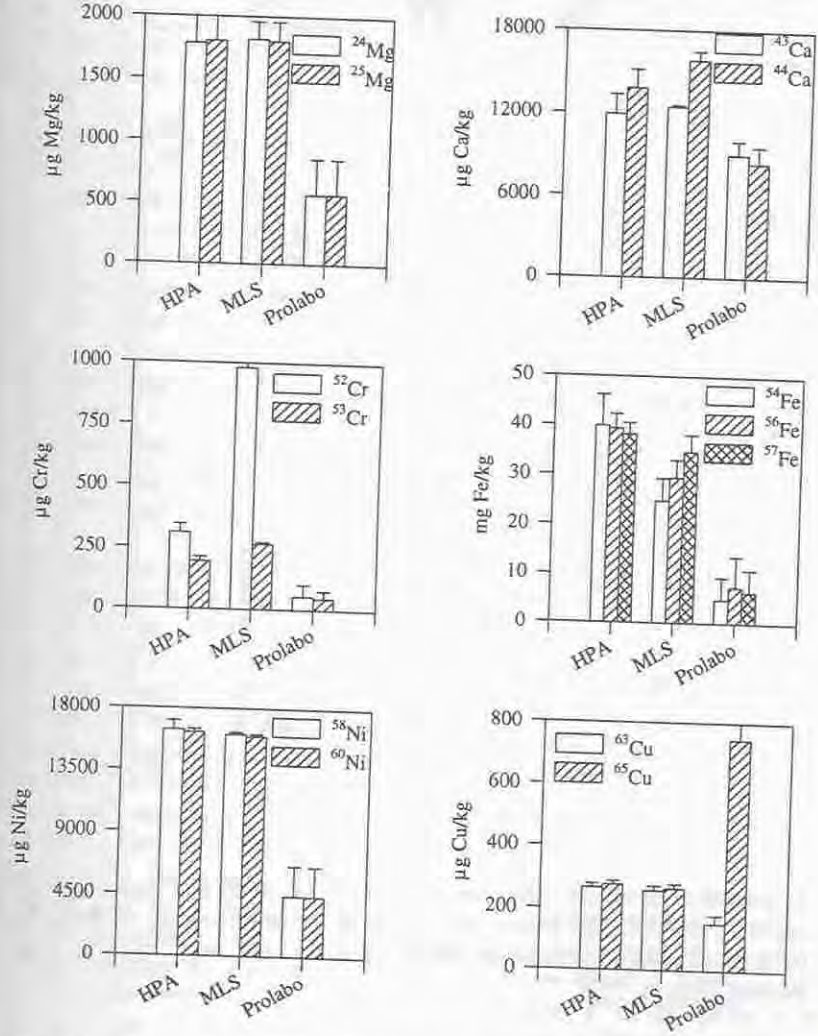

Figure 1a. Comparison of signal enhancement caused by molecular ions formed from digestion reagents and matrix components in the determination of trace elements by ICP-MS in the digests of the SRM 1634c obtained using the HPA, MLS, and Prolabo systems.

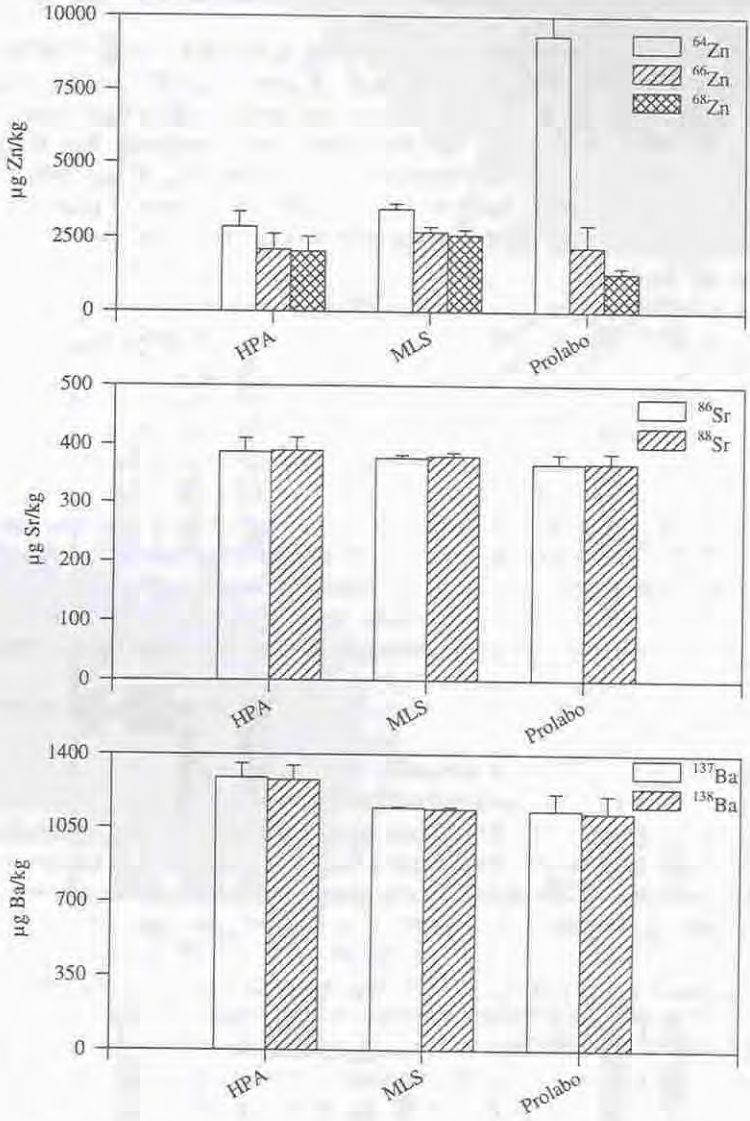

Figure 1b. Comparison of signal enhancement caused by molecular ions formed from digestion reagents and matrix components in the determination of trace elements by ICP-MS in the digests of the SRM 1634c obtained using the HPA, MLS, and Prolabo systems.

Fe. The isotopes of iron can suffer from polyatomic interferences: for instance, $^{40}Ar^{14}N^{+}$ and $^{37}Cl^{16}O^{1}H^{+}$ on ^{54}Fe, $^{40}Ar^{16}O^{+}$ on ^{56}Fe, and $^{40}Ar^{16}O^{1}H^{+}$ on ^{57}Fe. No systematic fluctuation in the signals of the iron isotopes, determined in the digests of the HPA or the Prolabo system, was

apparent from Figure 1a. However, the signals of Fe change in the order $^{54}Fe < {}^{56}Fe < {}^{57}Fe$ for the digests obtained with the MLS system. Carbon-based interference could be responsible for the increase in the intensity of ^{57}Fe, because the fuel oil digest obtained with the MLS system was characterized by high concentration of TOC. The internal standard (Sc) used for evaluating the concentration of elements could interfere ^{57}Fe due to $^{45}Sc^{12}C^{+}$. Although, ^{57}Fe is the preferred isotope for evaluating the concentration of iron in normal solution analysis, the fact that ^{57}Fe can suffer from carbon-based interference does not make it an isotope of choice for evaluating its concentration in matrices containing large concentrations of TOC.

Cu. The two isotopes of Cu (^{63}Cu and ^{65}Cu) gave similar signals for HPA and MLS systems whereas ^{65}Cu was much higher than ^{63}Cu in the digests of Prolabo (Figure 1b). Perhaps sulfuric acid based interfering ions, $^{32}S^{33}S^{+}$, $^{33}S^{16}O_2^{+}$, and $^{32}S^{16}O^{17}O^{+}$ could be responsible for such signal enhancement.

Zn. The signals for the three isotopes of zinc (^{64}Zn, ^{66}Zn, and ^{68}Zn) were compared in Figure 1b. The two isotopes, ^{66}Zn and ^{68}Zn, showed similar concentrations though the Prolabo system gave a slightly higher signal for ^{66}Zn. The signal for ^{64}Zn is higher than the signals for ^{66}Zn and ^{68}Zn in the digests of the three systems and this enhancement was pronounced in the digests of the Prolabo system. The zinc isotope, ^{64}Zn, is prone to interference from $^{32}S_2^{+}$ and $^{32}S^{16}O_2^{+}$. The recommended concentration of sulfur in the residual fuel oil SRM 1634c (20 g S/kg) may cause such an enhancement. Because of the additional contribution of sulfur-based interference in the Prolabo system a higher concentration for ^{64}Zn was observed. The higher relative concentration obtained for HPA and MLS systems when using ^{64}Zn compared with the concentration when using ^{66}Zn and ^{68}Zn in Figure 1b, is probably due to the fact that the much more abundant Ni (17540 µg/kg) has an isotope (^{64}Ni, abundance 1.16%) at mass 64.

Accuracy and precision

The concentrations of V, Co, Ni, As, and Se were certified in SRM 1634c by the National Institute of Standards and Technology (NIST), whereas an information value was given for Ba. To validate the results of the digestion procedures and to obtain confidence in the experimental data, a comparison of the values obtained when using the dissolution procedures was made with certified and recommended concentrations of the six trace elements in SRM 1634c (Table 4). The mean and standard deviations of five replicate determinations were calculated to evaluate the concentration of each element in SRM 1634c. The concentrations of V, Ni, and As determined in the digests obtained with the HPA and the MLS systems were comparable and were in acceptable agreement with those of the certified concentrations. Slightly lower values (~80%) were obtained for Co in the digests obtained with the HPA and the MLS systems. The certified concentration of Co (151 µg/kg) in the digested and diluted solutions (40 mL) was 0.94 µg/kg. This value is lower than the method determination limit and explains the lower accuracy achieved for Co. On the other hand, the Se concentrations measured were higher than the certified value. A dilution factor of 160 implies a real Se concentration below the MDL. There is a ^{82}Kr interference on ^{82}Se and probably this signal was measured. The experimentally found concentrations of Ba were highly comparable irrespective of the type of the digestion system used. However, they are lower than the recommended value of Ba. Ba and Sr are probably due to suspended inorganic particles ($BaSO_4$ from drilling fluids) in oil. Unlike the organically bound elements like V, Ni and Co, Ba and Sr do not suffer volatilization loss during Prolabo dissolution.

The concentration of the certified elements was lower than the certification value in the digests obtained with the Prolabo system. Furthermore, the experimentally found concentrations of trace elements in solutions obtained with the Prolabo digestion equipment were generally lower than the results of the HPA or the MLS digestion systems. This lack of accuracy and precision demonstrated by the Prolabo system is probably due to analyte loss by volatilization. Regardless of the mild digestion program used, the Prolabo system was unsuitable for the determination of trace elements in SRM 1634c (Table 4).

Table 4. Comparison of the certified and recommended concentrations of trace elements in SRM 1634c "Residual Fuel Oil" with the concentrations determined by ICP-MS in the digests of the HPA, the MLS, and the Prolabo systems (n = 5). The method determination limits (MDL, n = 3) achievable by each digestion system are included in the table.

	Concentration, µg/kg						
Isotope	HPA	MDL_{HPA}	MLS	MDL_{MLS}	Prolabo	$MDL_{Prolabo}$	Certified
^{9}Be	16 ± 3	4	34.9 ± 0.2	1.3	25 ± 1	0.4	
^{24}Mg	1780 ± 230	100	1820 ± 140	120	460 ± 200	290	
^{27}Al	2400 ± 800	86	1760 ± 90	200	< 2900	2900	
^{43}Ca	*11800 ± 1400	2700	12460 ± 710	1500	< 5300	5300	
^{51}V	26600 ± 500	6	26900 ± 960	0.8	17500±2600	55	28190 ± 400
^{53}Cr	200 ± 20	6	270 ± 7	15	< 30	34	
^{55}Mn	260 ± 20	40	250 ± 2	6	166 ± 18	9.8	
^{57}Fe	29850 ± 590	1390	28290 ± 360	200	16100±4300	1400	
^{59}Co	122 ± 2	36	120 ± 1	1.2	46.3 ± 6.4	2.8	151.00 ± 5.1
^{60}Ni	16260 ± 240	30	15940 ± 170	8	6600 ± 1300	70	17540 ± 210
^{63}Cu	266 ± 12	40	260 ± 10	11	150 ± 30	990	
^{66}Zn	2030 ± 500	360	2600 ± 180	100	1300 ± 200	330	
^{75}As	150 ± 7	60	170 ± 5	17	110 ± 20	46	142.6 ± 6.4
^{82}Se	170 ± 8	150	130 ± 7	67	< 260	260	102.0 ± 3.8
^{85}Rb	6.7 ±1.0	1	5.3 ± 0.5	0.7	< 20	20	
^{88}Sr	390 ± 20	0.7	380 ± 6	3	370 ± 20	40	
^{95}Mo	< 240	240	85 ± 1	13	59 ± 8	5.2	
^{107}Ag	< 10	10	< 0.6	0.6	< 1.4	1.4	
^{111}Cd	< 40	40	1.4 ± 0.3	0.5	< 3	3.2	
^{120}Sn	< 50	50	10.7 ± 0.7	6	< 2.8	2.8	
^{121}Sb	< 930	930	< 90	90	< 210	210	
^{125}Te	6.3 ± 0.6	3.3	< 3	3	< 4	3.6	
^{138}Ba	1280 ± 70	2.6	1140 ± 10	7	1120 ± 90	250	1800*
^{202}Hg	< 20	20	< 110	110	< 10	10	
^{205}Tl	< 40	40	< 5	5	< 2	2	
^{208}Pb	380 ± 14	90	410 ± 16	16	250 ± 40	130	
^{209}Bi	3.3 ± 0.3	1.6	1.5 ± 0.2	0.4	< 0.4	0.4	
^{238}U	6.3 ± 0.7	0.3	3.4 ± 0.1	0.1	< 1.7	1.7	

MDL- Method determination limits for HPA, MLS, and Prolabo systems. *Information value.

The precision of the three digestion systems was evaluated in terms of percent relative standard deviation (RSD) calculated on five measurements. Among the three digestion systems, the best precision was obtained with the MLS equipment, despite the incomplete decomposition of hydrocarbons in SRM 1634c (~1160 mg C/kg). The RSD values for the

MLS were less than 5% for most of the elements (Be, Al, V, Cr, Fe, Mn, Co, Ni, Cu, As, Sr, Mo, Ba, Pb, and U), less than 10% for a few elements (Mg, Zn, Se, Rb, Sn, and Bi), 25% for Cd, and 30% for Ca (Table 4). The HPA system assumes an intermediate position in terms of precision. With the HPA, RSD vales were ≤ 5% for eight elements (V, Co, Ni, Cu, As, Se, Ba, Pb), were ≤ 10% for seven elements (Cr, Mn, Fe, Sr, Te, Bi, and U), and were higher than 10% for Be, Mg, Al, and Ca. The Prolabo system generally gave highly imprecise results.

Method determination limits

The results of the method determination limits (MDL) calculated according to a modified equation (equation 1) of literature procedure [28] are summarized in Table 4.

$$\text{MDL} = 10\,\sigma \times \text{conc. } (\mu g/kg) \times \text{dilution factor}/(S-B) \quad (1)$$

where σ is standard deviation in counts of the blank solution. S is counts/s of a 10 or 100 μg element kg^{-1} of standard solution, B is counts/s of the blank solution.

The blank solution consisted of a mixture of HNO_3 and H_2O_2 (for HPA and MLS) or HNO_3, H_2O_2, and H_2SO_4 (for Prolabo) digested in a similar manner as the fuel oil (SRM 1634c). The highest MDLs were obtained for the Prolabo system as a result of which 13 elements (Al, Ca, Cr, Cu, Se, Rb, Mo, Sb, Te, Tl, Pb, Bi, and U) were below the determination limit. Although similar volumes of reagents were used in digestions with the HPA and MLS systems, generally the lowest MDLs were achieved for MLS. Five elements (Ag, Sb, Te, Hg, and Tl) were below the method determination limits in the digests of the MLS system and seven elements (Mo, Ag, Cd, Sn, Sb, Hg, and Tl) by the HPA system. The concentrations of only two elements (Sb and Tl) were found below the method determination limits in the digests of the three systems. The results further show the very important role played by sample preparation procedures. Generally, the method determination limits varied in the order MLS < HPA < Prolabo. The Prolabo system gave the highest MDLs probably because of increased blank levels from digestion reagents and partly from sulfur-based interference (for instance Zn). The MDLs for the majority of the elements (Table 4) are sufficiently low so that the experimentally determined concentrations for the HPA and the MLS systems (Table 4) provide valid results.

Contamination and analyte loss

The concentrations of Al and Fe in the digests of the high pressure asher were found to be higher than the concentrations measured in the digests of the other two systems. The high-pressure asher is vulnerable to contamination by Fe and Al seeing that the heating blocks are made of stainless steel or aluminium and can contaminate the digests in the silica digestion vessels. Under the conditions of digestion, the digestion chamber may become saturated with volatile compounds (for instance, $AlCl_3$, $FeCl_3$). When venting of digestion vessels takes place while the digestion program is in progress, contaminants in the vapor phase may find access to enter the digestion vessels. After the system had been cooled and the exhaust valve of the pressure chamber opened, the digestion vessels that were tightly closed, became loose and may have opened up further access for the contaminants present in the vapor phase. Such contamination was apparent for iron and aluminium because high RSD values (> 30%) were observed and the deviant data were rejected from both elements.

Generally, the concentrations of trace elements in the digests of the Prolabo system were very much lower than the concentrations in the digests of the MLS or the HPA system. Digestion procedures in open vessels are generally prone to loss of more volatile elements such as Hg, As, Se, Sb, Ni, and V [4,5]. In an extensive review of decomposition methods that employ the HNO_3-H_2SO_4 mixture in open vessels, the occurrence of complete or partial loss by volatilization of Hg, As, Se, Be, and Sb and mechanical loss as spray of Co, Fe, Cr, Cu, Mn, and Ni was reported [29]. The Prolabo system that is equipped with a reflux condenser would be expected to minimize volatilization losses. However, it is very likely that the prolonged evaporation stage (65 min at applied power of 99%) could have led to this loss of analytes. It is particularly the certified elements V, Co, Ni, As, and Se for which the loss is very significantly observed. In principle the MDLs achievable for the digests of the Prolabo equipment should be higher than the MDLs of the HPA or the MLS, because of the high blank values. However, lower MDLs were obtained for Be, Mo, Sn, and Tl indicating the likely loss of these elements from the blanks (Table 4).

CONCLUSION

The digestion parameters (reagent volume, reagent composition, digestion time, and applied power/temperature) that permit the destruction of the hydrocarbon matrix in SRM 1634c for the determination of trace elements were established for three digestion systems. The H_2SO_4 used to raise the temperature in the Prolabo digestion system introduced positive bias on the signals of elements prone to sulfur-based polyatomic interference (for instance, Cr, Cu, Zn, and Mo). Analyte loss due to volatilization, polyatomic interference from sulfuric acid, and high MDLs seriously limit the use of the Prolabo system for the determination of trace elements in SRM 1634c by ICP-MS. A further disadvantage of the Prolabo system included leakage of acid vapors despite the use of the ventilation system. The HPA system has more efficiently decomposed the hydrocarbon matrix. However, it was shown to be prone to contamination from the components of the digestion chamber and would not be the method of choice should Fe and Al be the analytes of interest. The degree of hydrocarbon destruction by the MLS digestion equipment was the least; however, the resulting digests were found suitable for the precise and accurate determination of trace elements by ICP-MS.

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REFERENCES

1. Siegmund, C.W. in *McGraw-Hill Encyclopedia of Science and Technology*, McGraw-Hill: New York; 1992; p 479.
2. Bettinelli, M.; Spezia, S.; Baroni, U; Bizzarri, G. *J. Anal. At. Spectrom.* **1995**, 10, 555.
3. Bettinelli, M.; Spezia, S.; Baroni, U; Bizzarri, G. *Mikrochim. Acta* **1996**, 123, 217.

4. Bettinelli, M.; Tittarelli, P. *J. Anal. At. Spectrom.* **1994**, 9, 805 and references therein.
5. Liu, J.; Sturgeon, R.E.; Willie, S.N. *Analyst* **1995**, 120, 1905.
6. Kingston, H.M.; Walter, P.J. *Spectroscopy* **1992**, 7, 20.
7. Bermejo Barrera, P.; Pita Calvo, C.; Bermejo Martinez, F. *Anal. Lett.* **1991**, 24, 447.
8. Olajire, A.A.; Oderinde, R.A. *Bull. Chem. Soc. Jpn.* **1993**, 66, 630.
9. Maranowsky, N.C.; Snyder, R.E.; Clark, R.O. *Anal. Chem.* **1957**, 29, 353.
10. Turunen, M.; Peräniemi, S.; Ahlgrén, M.; Westerholm, H. *Anal. Chim. Acta* **1995**, 311, 85.
11. Olsen, S.D.; Filby, R.H.; Brekke, T.; Isaksen, G.H. *Analyst* **1995**, 120, 1379.
12. Garavaglia, R.N.; Rodríguez, R.E.; Batistoni, D.A. *Fresenius J. Anal. Chem.* **1998**, 360, 683.
13. Olsen, S.D.; Westerlund, S.; Visser, R.G. *Analyst* **1997**, 122, 1229.
14. Borséki, J.; Knapp, G.; Halmos, P.; Bartha, L. *Mikrochim. Acta* **1992**, 108, 157.
15. Murillo, M.; Chirinos, J. *J. Anal. At. Spectrom.* **1994**, 9, 237.
16. Lord, C.J. *Anal. Chem.* **1991**, 63, 1594.
17. Polo-Díez, L.; Hernández-Méndez, J.; Pedraz-Penalva, F. *Analyst* **1980**, 105, 37.
18. Al-Swaidan, H.M. *Talanta* **1996**, 43, 1313.
19. Shott, J.E.; Garland, T.J.; Clark, R.O. *Anal. Chem.* **1961**, 33, 506.
20. Udoh, A.P.; Thomas, S.A.; Ekanem, E.J. *Talanta* **1992**, 39, 1591.
21. Ekanem, E.J.; Lori, J.A.; Thomas, S.A. *Talanta*, **1997**, 44, 2103.
22. Hernandez-Artiga M.P.; Muñoz-Leyva, J.A. *Analyst* **1992**, 117, 963.
23. Evans, E.H.; Ebdon, L. *J. Anal. At. Spectrom.* **1990**, 5, 425.
24. Knapp, G.; Panholzer, F.; Schalk, A.; Kettisch, P. in *Microwave-Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications*, Kingston, H.M.; Haswell, S.J. (Eds.); American Chemical Society: Washington, DC; 1997; p 423.
25. Knapp, G. *Fresenius Z. Anal. Chem.* **1984**, 317, 213.
26. Wondimu, T.; Goessler, W.; Irgolic, K.J. *Fresenius J. Anal. Chem.* **2000**, 367, 35.
27. Krachler, M.; Radner, H.; Irgolic, K.J. *Fresenius J. Anal. Chem.* **1996**, 355, 120.
28. Hewlett Packard, *Application Handbook HP 4500 Hardware and Performance*, Yokogawa Analytical Systems: Tokyo, Japan; pp 1-24.
29. Bock, R. *A Handbook of Decomposition Methods in Analytical Chemistry*, International Textbook Co.: London; 1979; p 215.