

Direct determination of metals in organics by inductively coupled plasma atomic emission spectrometry in aqueous matrices

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Abstract

A simple method for the simultaneous determination of up to 21 elements in organic matrices is proposed. Organic samples are simply dispersed in concentrated nitric acid by sonication, and the resulting emulsions/suspensions are directly aspirated into an inductively coupled plasma atomic emission spectrometer (ICP-AES) calibrated with aqueous standards for analysis. Proof of concept was provided by the excellent recoveries for the analysis of a 21-element metallo-organic standard. In addition, the results obtained using this method for a waste oil sample compared favorably with those from a method that utilized microwave digestion for sample preparation. Comparable results were also obtained by dilution in an organic solvent followed by ICP-AES analysis with an ultrasonic nebulizer equipped with a membrane desolvator. Furthermore, the viability and validity of this method were confirmed by the analysis of the National Institute of Standards and Technology standard reference material 1084a Wear-Metals in Lubricating Oil. Spike recoveries ranged from 83 to 105% and the limits of quantitation were $6 \mu\text{g g}^{-1}$ or less for all the elements analyzed.

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1. Introduction

The demand for metal content determination of organic liquids arises most frequently in petroleum products, pharmaceutical or industrial organic samples, and food products [1–29]. The metallic species may be present as soluble metallo-organic

compounds, colloids, or suspended as coarse or fine metallic particles. Atomic absorption spectrometry, a single element monitoring technique, was first used for the determination of metals in organics [16,18–26]. However, the development of the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS) techniques [30–38] has provided higher sensitivity, expanded linear dynamic range, simultaneous multi-element capability, low sample consumption, and high

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sample throughput. A wide range of organic samples have been analyzed by the ICP-AES, such as waste oils, solvent extracts, chromatography effluents or the organic solutions themselves [1–11,27,28].

Samples in organic matrices are traditionally converted to an aqueous state by digestion before introduction into an ICP-AES or an ICP-MS for analysis. The conventional ashing and acid dissolution methods are time-consuming and volatile elements may be lost [12–14]. Although microwave digestion methods in closed teflon vessels avoid volatilization losses [15], the risks of explosion and cross-contamination remain. Sanz-Segundo et al. [16] developed a multi-step microwave digestion method to process large samples and avoid the explosion hazard. Nevertheless, the method is still time-consuming, labor-intensive, and prone to incomplete digestion of the samples. Acid extraction of waste oil samples followed by drying and grinding was reported to give well-homogenized samples, which were then analyzed by X-ray fluorescence [17]. Emulsion sample preparation for the measurement of metals in lubricating oil has been reported [18–20], which somewhat simplified the sample preparation procedure since aqueous solutions can be used for the preparation of the calibration standards.

Direct determination of metals in non-aqueous solvents may be possible and reduces sample preparation time and avoids cross contamination; however, other difficulties arise from the wide range of densities, viscosities, flammability, and the increased care required for safe disposal. In addition, direct aspiration of an organic liquid normally requires additional equipment or techniques, such as using desolvation devices or introduction of oxygen in order to maintain the plasma. A flow of oxygen to the plasma also reduces molecular band emissions and prevents carbon build up within the torch and on the cooled cone; however, the performance of these methods is generally unsatisfactory due to high noise levels. Introduction of oxygen also produces polyatomic interferences for some elements in ICP-MS.

Electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) has been used by Escobar et al. [29] to eliminate

oxygen addition and reduce the organic matrix interference; however, the ETV parameters have to be optimized for each element thereby prolonging the procedure. In the authors' laboratory, it was found that due to the high sensitivity of ETV-ICP-MS, metal contamination of many organic solvents prevents their use in this technique. Toluene and xylene are good choices for this application; however, their high volatility makes quantitative measurements extremely difficult.

The purpose of this work was to find a simpler, faster, and more reliable way to determine metals in organic matrices without the use of organic solvents and without resorting to digestions.

2. Experimental

2.1. Reagents and materials

Trace metal grade concentrated nitric acid was purchased from Seastar (Sidney, BC, Canada). Deionized water was prepared by passing distilled water through a Milli-Q water system (Millipore Corporation, Bedford, MA). Isopropanol (IPA) and hydrogen peroxide (30%, certified ACS) were from Fisher Scientific (Fair Lawn, NJ). The OMS-21-XYL 21-element metallo-organic standard (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn) at $500 \mu\text{g g}^{-1} \pm 0.5\%$ in xylene, and the single element inorganic standards (1000 mg/l) were purchased from high-purity standards (Charleston, SC). NIST 1084a (wear-metals in oil, $100 \mu\text{g g}^{-1}$) was from National Institute of Standards and Technology (NIST, Gaithersburg, MD). Toluene (GR, Gibbstown, NJ) was purchased from EM Science. The actual waste oil sample was collected from a privately owned automobile.

The values reported in each table were the averages of 3–5 sample preparations/measurements of each sample.

2.2. Preparation of samples

2.2.1. Proposed direct analysis method

The OMS-21-XYL metallo-organic standard was prepared by transferring an aliquot of this

standard directly into concentrated nitric acid in a metal-free container followed by vigorous mixing.

Due to the high viscosities of the oil samples, they were first ‘liquified’ with a small portion of toluene and then suspended/dispersed in concentrated nitric acid with the aid of a sonicator followed by a water bath step at 80–90 °C for about 30 min following sonication. If the prepared oil samples were not immediately analyzed, a small amount of residual oily organic matter from the oil may appear floating on the solution surface. It was found that this would not affect the recoveries of the elements determined.

Before bringing to the final volume, yttrium was added to all samples as internal standard to give a final concentration of 1.0 $\mu\text{g ml}^{-1}$.

2.2.2. Microwave digestion method

Portions of the two oil samples were also microwave digested with 5 ml of concentrated nitric acid and 2 ml of hydrogen peroxide using the heating program listed in Table 1. The digested solutions were then quantitatively transferred to 50-ml volumetric flasks and diluted to volume with 80% HNO_3 after yttrium was added as internal standard. The concentration of yttrium in the prepared samples is also 1.0 $\mu\text{g ml}^{-1}$.

2.2.3. Direct organic solvent dilution/ultrasonic nebulizer method

The sample was directly dissolved in isopropanol/toluene mixture (8:2, v/v). The use of isopropanol (IPA) in the mixture, instead of neat toluene, was to prolong the peristaltic tube (solvent resistant) life. The use of this mixture also reduced the volatility of the solvent since solvent evaporation became less of an issue compared to

Table 2

Perkin–Elmer optima 3300 DV ICP-AES instrument conditions and measurement parameters

RF power	1350 W
Plasma gas flow	15 l min ⁻¹
Auxiliary gas flow	0.5 l min ⁻¹
Nebulizer gas flow	0.8 l min ⁻¹
Plasma view	Axial
Sample introduction	Cross-flow nebulizer with Scott spray chamber
Sample pump tubing	Black/black
Sample uptake rate	1.5 ml min ⁻¹
Wavelength (nm)	
Ag	328.068
Al	396.153
B	208.957
Ba	455.403
Ca	317.993
Cd	228.802
Cr	267.716
Cu	324.752
Fe	259.939
Mg	285.213
Mn	259.372
Mo	203.845
Na	589.592
Ni	232.003
P	178.221
Pb	261.418
S	180.663
Si	251.611
Sn	283.998
Ti	334.940
V	292.402
Zn	213.856

the use of the neat toluene as the solvent. Although the equipped membrane desolvator with the ultrasonic nebulizer (USN) removed the bulk of the solvent, a small stream of oxygen was still needed to prevent carbon build-up in the ICP assembly.

Table 1

Milestone microwave digestion program

Step	Time (min)	Power (W)
1	1	250
2	2	0
3	8	250
4	5	400
5	15	500

2.3. Preparation of standards

The standards used in direct organic solvent dilution/USN method were prepared by diluting the stock standards prepared in xylene with an isopropanol/toluene mixture (8:2, v/v). For the rest of the analysis, the calibration standards were prepared by serial dilutions and mixings of single-

Table 3
CETAC U-6000AT⁺ USN operating conditions

Oxygen flow	0.030 l min ⁻¹
Sweep gas flow	1.40 l min ⁻¹
Desolvator heater temperature	150 °C
USN heater temperature	130 °C

element stock standard solutions in 80% or concentrated nitric acid solutions. In all of the working calibration standards made in 80% nitric acid or made in concentrated nitric acid, yttrium was also added as internal standard at 1.0 µg ml⁻¹.

2.4. Instrumentation

A milestone MLS 1200 mega high performance microwave digestion unit, a Perkin–Elmer Optima 3300 DV ICP-AES, and a CETAC U-6000 AT⁺ USN were used in this study. The relevant instrumental conditions and operating parameters are listed in Tables 1–3, respectively. In addition, a Haake SWB-25 water bath unit was also used.

3. Results and discussion

A direct analysis method has been developed in which the organic samples are dispersed in concentrated nitric acid with sonication and heating. A metallo-organic standard containing 21-element, the NIST standard reference material (SRM) 1084a Wear-Metals in Lubricating Oil, and a waste oil sample from a private automobile were suspended/dispersed evenly in concentrated nitric acid and then directly analyzed by ICP-AES using the proposed direct analysis method without any other chemical pretreatments. This direct analysis method was compared to the ICP-AES method using microwave digestion as the sample preparation step, and to the ICP-AES method using an USN with a membrane desolvator to introduce samples dissolved directly in organic solvent mixture.

3.1. The analysis of the OMS-21-XYL metallo-organic standard

As a proof-of-concept, the OMS-21-XYL metallo-organic standard was analyzed as a sample using the proposed direct analysis method. An aliquot of 20–50 µl of the sample was transferred to a polypropylene centrifuge tube, and the weight of the sample was recorded. Into this tube, an aliquot of 20 ml concentrated nitric acid was added followed by sonication for about 15 min. Then the samples were heated in a water bath at 80–90 °C for about 30 min following sonication. The samples were then analyzed against a calibration obtained with working standards prepared with aqueous stock standard diluted in concentrated nitric acid. The results are given in Table 4. The recoveries of all elements were ≥ 75%, with most being higher than 90%.

3.2. The analysis of the NIST standard reference material 1084a Wear-Metals in Lubricating Oil

The feasibility of the proposed direct analysis method was further demonstrated by the analysis of the NIST SRM 1084a Wear-Metals in Lubricating Oil. The results obtained are shown in Table 5. The results showed that the recoveries of the 13 elements monitored were ≥ 70% with most elements recovering higher than 90%.

3.3. The analysis of the NIST 1084a with more traditional sample preparation methods: microwave digestion/direct dilution

For comparison, NIST 1084a was also analyzed by ICP-AES after microwave digestion. The results are given in Table 6. With the exception of Si, which had a recovery of 64%, the rest of the elements recovered from 87 to 105%.

The NIST 1084a Wear-Metals in Lubricating Oil was also analyzed by ICP-AES coupled to an USN equipped with a membrane desolvator. The analytical results are also given in Table 6. The proposed direct analysis method provides comparable results to those obtained by using the ICP-AES/USN method and to those obtained with the ICP-AES/microwave digestion method. Whereas,

Table 4
The analysis of OMS-21-XYL ($500 \mu\text{g g}^{-1}$)

Element	Measured conc. ($\mu\text{g g}^{-1}$)	Recovery (%)
Ag	516 ± 13	103
Al	551 ± 21	110
B	413 ± 16	83
Ba	514 ± 11	103
Ca	1250 ± 316	250
Cd	507 ± 7	102
Cr	500 ± 5	100
Cu	554 ± 5	111
Fe	532 ± 12	106
Mg	502 ± 11	100
Mn	530 ± 11	106
Mo	530 ± 2	106
Na	479 ± 32	96
Ni	514 ± 11	103
P	–	–
Pb	501 ± 6	100
Si	918 ± 112	184
Sn	503 ± 7	101
Ti	378 ± 6	76
V	536 ± 11	107
Zn	509 ± 12	102

the proposed direct analysis method offers the advantages of an easy and rapid sample preparation, relatively free from cross-contamination commonly seen with microwave digestion, and the use of aqueous standards for instrument calibration. The proposed direct analysis method also maintains an organic solvents-free ICP system, requiring fewer accessories and easier waste handling and disposal.

3.4. The analysis of an actual waste engine oil

A waste engine oil sample from a private automobile was collected and analyzed using the proposed direct analysis method, the microwave digestion method, and the ICP-AES/USN method with the sample dissolved in isopropanol/toluene mixture (8:2, v/v). The results are compiled in Table 7. In this particular sample, with the exception of Fe, Mg, B, Ca, Si and Zn, the majority of the elements are present at less than $5 \mu\text{g g}^{-1}$. Several elements were not determined by

Table 5
The analysis of the NIST 1084a Wear-Metals in Lubricating Oil with the proposed method

Element	Certified value ($\mu\text{g g}^{-1}$)	Measured value ($\mu\text{g g}^{-1}$)	Recovery (%)
Ag	104 ^a	95 ± 0.9	91
Al	101.4 ± 1.5	88 ± 0.9	87
Cr	98.3 ± 0.8	81 ± 0.1	83
Cu	100 ± 1.9	103 ± 1	103
Fe	98.9 ± 1.4	93 ± 0.1	94
Mg	99.5 ± 1.7	83 ± 0.6	83
Mo	99.5 ± 1.4	92 ± 0.7	92
Ni	99.7 ± 1.6	102 ± 1.2	102
Pb	101.1 ± 1.3	96 ± 2.4	95
Si	103 ^a	94 ± 4.9	91
Sn	97.2 ± 2.6	95 ± 5.3	98
Ti	100.4 ± 3.8	70 ± 0.4	70
V	95.9 ± 9.4	95 ± 0.3	100

^a Reference values.

the microwave digestion method due to high background from contaminations. Frequently, the levels of these elements that were leached out of the vessels were at or exceeded the levels of elements present in the digested samples. This was confirmed by the analysis of the sample digestion blanks. Although this problem can be minimized by repeated digestion of the method blanks with the vessels, it is rather time-consuming.

Some elements were also not determined in the ICP-AES/USN method, since only those elements that have certified or reference values in the NIST 1084a Wear-Metals in Lubricating Oil were used in the preparation of calibration standards. Excellent agreement was achieved for the Fe level (which is the major indicator of the extent of engine wear) in this sample, by all three methods in this study.

3.5. Spike recoveries, precision (RSDs), limits of detection and the limits of quantitation

The limits of detection (LODs), the limits of quantitation (LOQs), and the method precisions (RSDs) of the proposed direct analysis method were determined from spike recovery measurements.

Table 6
The analysis of the NIST 1084a with traditional sample preparation methods

Element	NIST 1084a Wear-Metals in Lubricating Oil ($\mu\text{g g}^{-1}$)				
	Certified or value	Microwave digestion		USN	
		Result	Recovery (%)	Result	Recovery (%)
Ag	104 ^a	96 \pm 3	92	88 \pm 1	85
Al	101.4 \pm 1.5	88 \pm 4	87	94 \pm 2	93
Cr	98.3 \pm 0.8	100 \pm 0.3	102	94 \pm 2	96
Cu	100 \pm 1.9	99 \pm 0.9	102	93 \pm 2	93
Fe	98.9 \pm 1.4	104 \pm 4	105	96 \pm 1	97
Mg	99.5 \pm 1.7	96 \pm 7.4	96	94 \pm 1	94
Mo	99.5 \pm 1.4	103 \pm 1	103	76 \pm 1	76
Ni	99.7 \pm 1.6	98 \pm 0.9	98	91 \pm 2	91
Pb	101.1 \pm 1.3	99 \pm 4	98	96 \pm 2	95
S	1700 ^a	1690 \pm 90	99	–	–
Si	103 ^a	66 \pm 7	64	111 \pm 3	108
Sn	97.2 \pm 2.6	92 \pm 12	95	93 \pm 1	96
Ti	100.4 \pm 3.8	101 \pm 1	101	99 \pm 2	99
V	101 \pm 9.4	101 \pm 0.8	100	82 \pm 4	81

^a Reference values.

Table 7
The comparison of the results of the waste engine oil sample obtained by various methods

Element	The propose method ($\mu\text{g g}^{-1}$)	Microwave digestion ($\mu\text{g g}^{-1}$)	USN/ICP-AES ($\mu\text{g g}^{-1}$)
Ag	< 5	< 5	< 5
Al	< 5	< 5	< 5
B	39 \pm 0.3	Not determined	Not determined
Ba	< 5	< 5	Not determined
Ca	306 \pm 3	Not determined	Not determined
Cd	< 5	< 5	< 5
Cr	< 5	< 5	< 5
Cu	< 5	< 5	< 5
Fe	16 \pm 0.3	15 \pm 0.1	16 \pm 3
Mg	432 \pm 25	Not determined	392 \pm 28
Mn	< 5	< 5	< 5
Mo	< 5	< 5	< 5
Na	< 5	Not determined	Not determined
Ni	< 5	< 5	< 5
Pb	< 5	< 5	< 5
Si	107 \pm 1	Not determined	Not determined
Sn	< 5	< 5	< 5
Ti	< 5	< 5	< 5
V	< 5	< 5	< 5
Zn	40 \pm 0.3	Not determined	Not determined

Table 8
Spike recoveries, precision (RSDs), LODs and LOQs of the proposed method

Element	Spike recovery (%)	Precision (% RSD)	LOD ($\mu\text{g g}^{-1}$)	LOQ ($\mu\text{g g}^{-1}$)
Ag	93 \pm 0.3	1.1	0.3	1.1
Al	100 \pm 1	1.5	0.6	1.9
B	83 \pm 1	2.2	N/A	N/A
Ba	102 \pm 1	0.9	0.5	1.6
Ca	N/A	N/A	N/A	N/A
Cd	95 \pm 3	1.5	0.4	1.5
Cr	98 \pm 3	0.8	0.1	0.3
Cu	105 \pm 2	1.9	0.8	0.8
Fe	90 \pm 2	1.3	0.3	1.0
Mg	N/A	N/A	N/A	N/A
Mn	96 \pm 0.4	0.9	0.3	1.0
Mo	95 \pm 1.2	3.1	0.4	1.3
Na	99 \pm 5	5.8	0.5	1.6
Ni	98 \pm 3	2.9	0.9	3.1
Pb	87 \pm 2	2.4	1.7	5.6
Si	N/A	N/A	N/A	N/A
Sn	88 \pm 5	5.6	1.5	5.2
Ti	95 \pm 1	1.0	0.3	1.0
V	95 \pm 1	1.1	0.4	1.2

An aliquot of the waste engine oil sample was suspended/dispersed in concentrated nitric acid solution as described in Section 2, and then spiked with the $0.1075 \mu\text{g g}^{-1}$ metallo-organic standard prepared by diluting the OMS-21-XYL with the isopropanol/toluene mixture (8:2, v/v). The recoveries for all elements ranged from 83 to 105%. The recovery data for Ca, Mg and Si were not given since their concentrations in this waste oil before the spiking were too high relative to the spiked levels. The LODs and LOQs of the proposed direct analysis method were evaluated by spiking and measuring 11 aliquots of the waste engine oil with the same $0.1075 \mu\text{g g}^{-1}$ metallo-organic standard. The LODs are defined as three times the standard deviations of the 11 measurements, and the LOQs, ten times the standard deviations of the 11 measurements. The method accuracy for each element is estimated by the relative standard deviations (RSDs) of the same 11 measurements. The results are given in Table 8. It is shown that the precision of the method for all elements is less than 6% RSD, and the LOQs of the method for all elements are less than $6.0 \mu\text{g g}^{-1}$.

4. Conclusions

Comparable results from more traditional methods used in this study demonstrate that metals in organics can be accurately analyzed by with the proposed direct analysis method, and lengthy and contamination-prone digestion or the use of organic solvents can be avoided. The sample preparation procedure is simpler, less time-consuming, and less labor-intensive. An additional advantage of the proposed direct analysis method is that the calibration standards can be prepared in concentrate nitric acid with readily accessible aqueous inorganic stock standards.

This method is suitable for the determination of metals in a majority of organic solvents or matrices.

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