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The Use of Emulsions for the Determination of Mg, Al, Ti, V, Mn, Ni, Mo, Cd, and Pb in Oils by Inductively Coupled Plasma Mass Spectrometry(ICP-MS).

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إستخدام المستحلبات لقياس تركيز بعض العناصر المعدنية في الزيوت بواسطة جهاز مطياف الكتلة – بلازما الحث المباشر

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تم في هذه الدراسة التحقق عمليا من إمكانية الحقن المباشر للزيوت في صورة مستحلب متجانس لغرض قياس تركيز بعض العناصر المعدنية بها بواسطة جهاز مطياف الكتلة – بلازما الحث المباشر كبديل للطرق التقليدية الشائعة في المعالجة الكيميائية الأولية (الحرق الجاف، التليين بواسطة الأحماض، الاستخلاص بالمذيبات العضوية، التخفيف بالمذيبات العضوية وغيرها) لمثل هذا النوع من العينات، استهدافا منا لتفادي الكثير من العيوب الملازمة لهذه الطرق لما لها من تأثير مباشر على الدقة والسرعة في إجراء عملية القياس إجمالا.

اعتمدت هذه المنهجية على إجراء كيميائي بسيط ألا وهو استحلاب عينات الزيت في الماء بواسطة عامل الاستحلاب Triton X-10 وإدخال هذا المستحلب مباشرة إلى البلازما للقياس.

بالنظر إلى التركيب الكيميائي المعقد للزيوت تعتبر النتائج المتحصل عليها جيدة من وجهة النظر التحليلية وبالمقارنة مع عيوب الطرق الشائعة أثبتت الدراسة إمكانية تبني هذه الطريقة المستحدثة في التحليل الكمي الروتيني للعناصر المعدنية في الزيوت مما يوفر الجهد والوقت إلى جانب الكلفة والدقة في القياس.

Abstract : *Direct analysis of emulsified organic samples by inductively coupled plasma mass spectrometry (ICP-MS) reduces sample preparation time considerably and avoids the loss of volatile elements that can occur during ashing and heating stages of digestion. A simple procedure has been evaluated in terms of its analytical performance for the determination of trace elements in oil samples by ICP-MS. The technique is based on emulsifying the oil samples in water using Triton X-100 as surfactant .The oil samples introduced directly into the plasma in the form of oil-in-water emulsion. Optimisation of the chemical conditions of the emulsion is reported. Method validation was performed by analysing Certified Reference Material CRM used oil HU1 for (SCP Science) and 1084a wear metals in lubricating oils (NIST). Satisfactory accuracy was obtained for Mg, Al, Ti, V, Mn, Ni, Mo, Cd and Pb in. The precision of the emulsion methodology was better than 8 % for most elements. Comparison of the method with acid digestion technique showed good agreement, validating the methodology and confirmed its applicability for routine analysis. The method detection limits for Mg, Al, Ti, V, Cr, Mn, Ni, Mo, Cd and Pb were 0.1, 0.06, 0.1, 0.06, 0.1, 0.02, 0.03, 0.1, 0.03 ng/ml respectively, indicating that the method is performing well for organic matrices containing very low concentrations of trace elements.*

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INTRODUCTION

Accurate measurements of trace elements concentration in a wide variety of organic based materials is essential to the petroleum industry for corrective actions during oil production and refining to prevent catalyst poisoning, corrosion, scale formation and assessment of environmental pollution. Modern instrumental techniques such as Inductively coupled plasma mass spectrometry (ICP-MS) have been widely used for such measurements and considered the technique of choice for the determination of trace metals in oils, it is an extremely sensitive technique with detection limits in parts per trillion (ppt) for many elements in aqueous solutions. It provides simultaneous multi-element capability, low sample consumption and high sample throughput. The advantages of ICP-MS include elemental and isotopic analysis for major, minor trace and ultra trace concentration levels for a wide variety of sample materials, used in geological and environmental science, nuclear and semi-conductor industries, material science, medicine, agriculture, oil industry food and biological science.

Commonly, for the analytical determination of metallic elements in crude oils and petroleum products by ICP-MS, different sample treatment procedures have been used. These include dry ashing, acid digestion, dilution with suitable organic solvent and extraction methods. In most cases those pretreatment procedures are tedious and time consuming with the consequent risk of sample contamination and analyte loss.

Recently, emulsion sample preparation/ introduction methodology has been reported for the determination of trace elements by ICP-MS in various organic samples as an alternative means [1,2,3,4] to overcome the drawback of traditional methods.

"Direct emulsification of oil sample with surfactants provides a rapid methodology for sample preparation since this approach does not require any destruction of the organic matter. It simply reduces the viscosity of the sample solution, and evenly disperses the oil in the water phase, making the properties of the oil emulsion close to those of an aqueous solution" [5].

In this work the proposed emulsion methodology was validated for determination of Mg, Al, Ti, V, Mn, Ni, Mo, Cd, and Pb and cross validated by acid digestion technique. However, it is important to remember that the methodology was evaluated not only taking into account validation parameters such as accuracy, precision and limits of detection achieved but also the crucial practical consideration such as time to complete the analysis, sample contamination, costs and eventually the practicability for routine use.

EXPERIMENTAL WORK

1. Instrumentation

Hewllet Packard 4500 quadruple inductively coupled plasma mass spectrometry equipped with Babington nebulizer was used in this study. The instrumental and operational parameters are listed in Table 1. Argon (99.95 %) was used as the plasma gas. The aqueous and emulsion solutions were introduced into the plasma by a peristaltic pump.

2. Reagents

All reagents were of the highest available purity except where stated. Ultra pure water was obtained from a USFELGA model (Option 7). Multi element working standards solutions were freshly prepared as required from individual element stock standards solutions used for calibration purpose were prepared by suitable dilution of the stock standards solutions and emulsion mixture. All glassware was treated

Table1. Hewlett Packard 4500 ICP-MS operational parameters.

Rf power	1250 w	Number of replicate	3
Carrier gas	1.21 /min.	Calibration mode	External calibration
Peripump	0.2 rps	Curve fit	Linear through zero
Auxiliary gas flow	12.6 l/min	Plasma gases	All Argon
Carrier gas pressure	557.0 kpag	Peristaltic pump parameters:	
Spray chamber	water cooled 2.0 C°	uptake speed	0.5 rps
Measurements time	30 sec.	up take time	30 sec.
Acquisition time	19.2600 sec.	stabilize time	30 sec.
Nebulizer	Babington nebulizer		

overnight with 10% nitric acid and rinsed with abundant deionised water prior to use. Tetraline (1, 2, 3, 4-tetrahydronaphthalene) supplied by Fluka AG was used as the co-solvent and Triton X-100 (Iso octylphenoxy poly ethoxy ethanol) supplied by BDH Pool England was used as the emulsifying agent employed. ARISTAR grade nitric acid 96% Sp.g. 1.42, sulphuric acid 98% Sp.g. 1.84 and hydrogen peroxide 30% supplied by BDH were used. Validation of the developed method was performed with Certified Reference Material (HU-1, used oil supplied by SCP Science) and SRM1084a wear metals in lubricating oils supplied by National Institute of Standards and Technology (NIST).

3. Sample Pre-Treatment

Oil-in-water emulsions were prepared in the following manner; 0.1g of oil sample weighed into a 100ml volumetric flask, equivalent weight of Tetralin was added. The mixture then agitated mechanically until a homogeneous solution is obtained. 0.3g of Triton X-100 then added to the mixture followed by vigorous agitation until a homogeneous solution phase produced again. About 5 ml of deionised water was added drop wise with continues agitation. Finally, the solution made-up to the mark with deionised water.

RESULTS AND DISSCUSION

To estimate the optimum conditions for the formation of a homogeneous and stable emulsion, the ratio of oil to Triton X-100 was varied. Emulsion solutions ratio were prepared by mixing oil, Tetralin, and surfactant respectively as follows: (0.1**:** 0.1 **:** 0.1g), (0.1 **:** 0.1 **:** 0.2g), (0.1 **:** 0.2 **:** 0.2g), (0.1 **:** 0.2**:** 0.3g), (0.1 **:** 0.1 **:** 0.3g), (0.1 **:** 0.2 **:** 0.5g).

Because of the relatively higher concentrations of most elements in the oil samples, 0.1g was selected as an optimum weight for analysis to avoid excessive sample consumption. Visual inspection of the emulsions showed that visible oil droplets could be observed in the mixture containing 0.2g of Triton X-100 which is unsuitable for introduction into the plasma. Whilst for the emulsion containing 0.1g of Triton X-100 small quantity of the oil was never emulsified.

In contrast visually stable and homogeneous emulsion with finest droplets of the oil was obtained with one containing 0.3g of Triton X-100. Therefore, 0.3g TritonX-100 was chosen as the optimum concentration for the preparation of emulsion samples in this study. Taking into account, that the emulsion coalesced in about twenty minutes but easily could be reconstituted by shaking, therefore the emulsion was practically stable for acceptable period of time enabling to perform the measurements (in triplicate).

Certified reference materials (CRM) are often the best tool to verify the accuracy of analytical methods. Consequently, the accuracy of the proposed method was assessed by analysing the CRM (Used oil HU-1) and further investigated by SRM 1084a (Wear metals in lubricating oils).

Tables 2 and 3 summarizes mean concentrations of determined elements and observed percentage errors (E%) of both CRM and SRM taking into consideration the complex sample matrix of the oil .In our opinion these results indicating an adequate accuracy. Because when using CRM it should be remembered that all analytical results have inherent uncertainties due to both random and systematic effects. It is therefore unlikely that the results obtained by a method when measuring a CRM will be exactly

Table 2. Mean concentrations obtained on CRM (HU-1) emulsion and acid digestion samples; the percentage error (E %) and certified values is also included .

	Accuracy			Precision (RSD %)*		
Element	Emulsion	E% E%	Acid digestion	Emulsion	Acid digestion	Certified value
Mg	9.0	- 18.2	11.8	2.2	2.7	11
Al	12.0	- 14.2	12.3	4.8	3.5	14
Ti	8.5	- 5.5	12.9	6.7	5.3	9.0
V	6.1	- 12.8	8.4	5.9	1.1	7.0
Cr	13.4	- 10.6	17.6	1.0	1.0	15
Mn	17.1	- 5.0	19.7	1.8	1.5	18
Ni	44.1	- 2.0	43.5	2.6	7.8	45
Mo	11.0	0.0	8.1	1.3	0.3	11
Cd	15.0	0.0	14.9	1.7	3.0	15
Pb	19.3	- 3.5	17.6	1.8	1.2	20

*RSD = Relative standard deviation; all concentrations in mg/kg ; number of replicate= 6.

Table 3. Mean concentrations obtained on SRM 1084a emulsion samples ; the percentage error (E %) and certified value is also included.

Element	Emulsion	E (%)	Precision (% RSD)	Certified values
V	107.0	11.5	9.0	95.9
Ni	99.6	- 0.1	7.9	99.7
Cu	104.7	4.7	5.8	100.0
Pb	102.4	1.3	5.4	101.1
Ti	98.1	- 2.3	5.2	100.4
Mo	106.5	6.1	4.7	100.3
Mg	101.0	1.5	6.3	99.5

RSD = Relative standard deviation ; all concentrations in µg/g; number of replicate = 4.

the same as the certified value of the CRM. What is important is that the results obtained are within an acceptable tolerance limit for the end use requirement of the method and therefore no need for any more formal demands [6].

As the further verification of analytical method performances were made by the acid digestion procedure. It can be seen fromTable 2 that the comparison of the results between the two techniques was similar and reasonable agreements for all elements with no significant deviations observed.

It is noteworthy that the agreement of the results of emulsion is found to be good for most targeted elements when compared to the certified values. Confirming the accuracy of the emulsion methodology and validating it in general as a simple way of direct introducing of organic type samples into ICP-MS.

The long-term precision for each element was estimated by the percent relative standard deviation (%RSD) obtained by assessing several emulsion samples prepared and analysed over a 3 month period. Tables 2 and 3 give also the precision for each element estimated for CRM (HU-1) and SRM (1084a). An indication that the developed procedure can produce precise results for heterogeneous mixtures such as oils.

Acid Digestion Versus Emulsion Technique

The basic assumption to be made is that the emulsion and acid sample digestion procedures can be evaluated as a function of the time involved in the preparation of the samples and the time needed to complete the whole measurement process. The emulsion sample preparation takes approximately 15 minutes compared with at least 1 hr for sample digestion. Moreover, the number of samples that can be digested at the same time limits the sample throughout.

Limit of Detection (LOD)

Table 4 gives the calculated detection limits based on three times the standard deviation(SD) of the blank signals, n =10. The blank prepared in the same way as the samples, but without oil added (0.1g Tetralin + 0.3g Triton X-100). These limits of detection show the suitability of the method for matrices containing very low concentrations of trace elements.

Table 4. Method detection limits.

Element	LOD ng/ml
Mg	0.15
Al	0.06
Ti	0.18
V	0.06
Mn	0.15
Ni	0.02
Mo	0.03
Cd	0.12
Pb	0.03

Calibration and Internal Standardization

The analytical interest of this study was to check the possibility of using aqueous calibration solutions to quantify CRM samples. Therefore, the external calibration technique was used with internal standardization (indium reference solution -^{115}In) at 50ppb to assess the impact of any interfering compounds and detect any signal variations due to transport efficiency.

The calibration curves of the emulsified aqueous standards (Fig. 1) reveals that the calibration process was certainly under control. The slops and intercepts of all calibration curves did not differ significantly from the ideal values of 1 and 0, respectively.

The internal standard was performing well as the analytical standards. The acceptable relative error of measurements suggested that there were no significant matrix effects. This is quite logical considering that approximately 98 % of the emulsion is aqueous phase as a result the emulsion possesses interestingly a similar nature and behaviors of the aqueous standard solution.

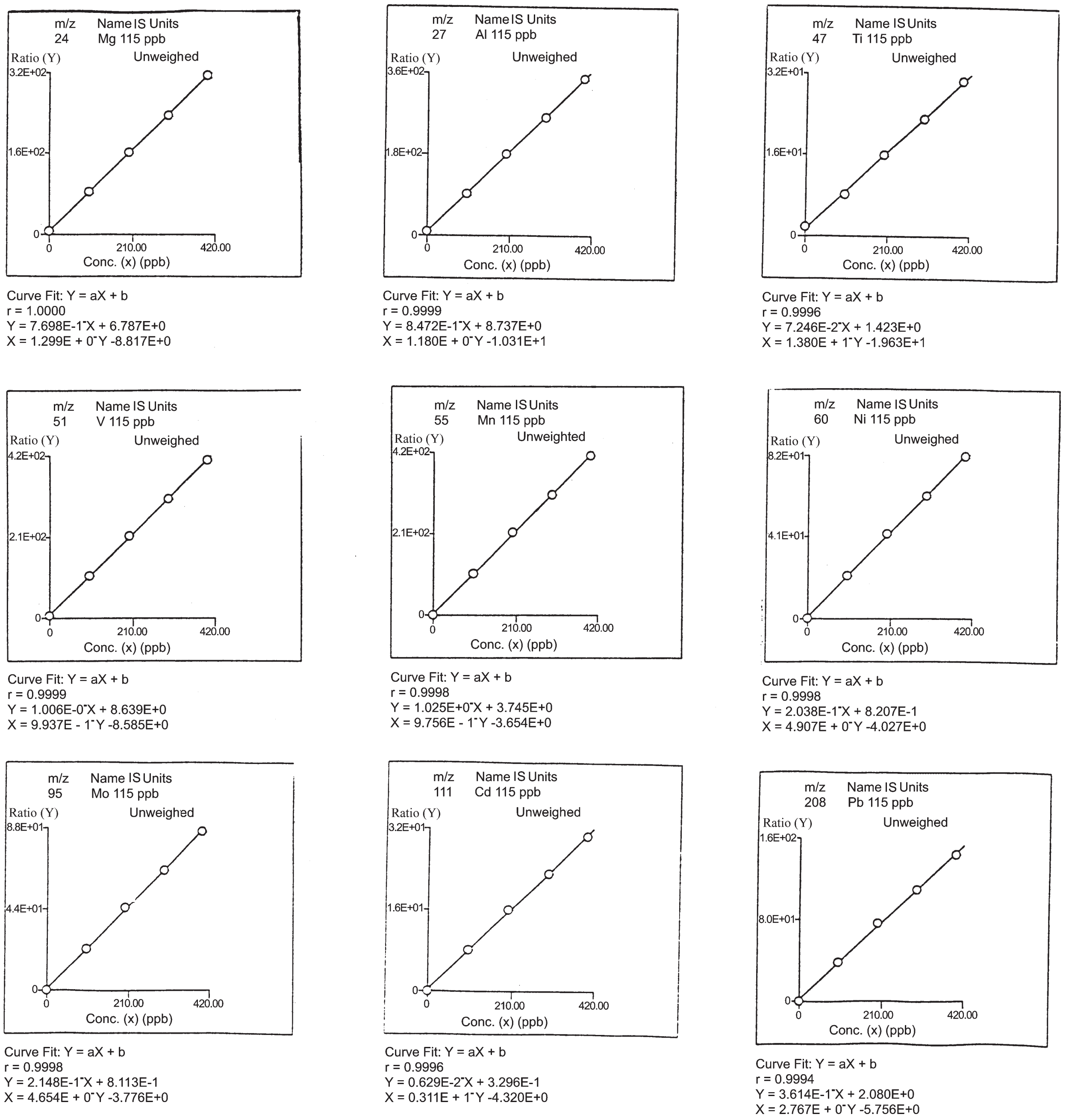
The absence of any matrix effect or any change in transport efficiency however encouraged us therefore to use the aqueous calibrations process.

Table 5 presents the results obtained of analysing the emulsified CRM (used oil HU-1) samples using

Table 5. Analysis of CRM emulsions samples (used oil HU-1) by two different calibration methods.

Element	Aqueous standards	E %	Emulsified standards	E %	Certified values
Mg	8.2	- 15	9.0	-18.2	11.0
Al	11.8	- 15	12.0	-14.2	14.0
Ti	9.3	3.3	8.5	- 5.5	9.0
V	7.9	12.8	6.1	-12.8	7.0
Mn	18.2	1.1	17.1	- 5.0	18.0
Ni	45.8	1.7	44.1	- 2.0	45.0
Mo	12.3	11.8	11.0	0.0	11.0
Cd	15.0	0.0	15.0	0.0	15.0
Pb	18.9	- 5.5	19.3	- 3.5	20.0

All concentrations in mg/kg



Curve Fit: Y = aX + b
r = 1.0000
Y = 7.698E-1¯X + 6.787E+0
X = 1.299E + 0¯Y -8.817E+0

Curve Fit: Y = aX + b
r = 0.9999
Y = 8.472E-1¯X + 8.737E+0
X = 1.180E + 0¯Y -1.031E+1

Curve Fit: Y = aX + b
r = 0.9996
Y = 7.246E-2¯X + 1.423E+0
X = 1.380E + 1¯Y -1.963E+1

Curve Fit: Y = aX + b
r = 0.9999
Y = 1.006E-0¯X + 8.639E+0
X = 9.937E - 1¯Y -8.585E+0

Curve Fit: Y = aX + b
r = 0.9998
Y = 1.025E+0¯X + 3.745E+0
X = 9.756E - 1¯Y -3.654E+0

Curve Fit: Y = aX + b
r = 0.9998
Y = 2.038E-1¯X + 8.207E-1
X = 4.907E + 0¯Y -4.027E+0

Curve Fit: Y = aX + b
r = 0.9998
Y = 2.148E-1¯X + 8.113E-1
X = 4.654E + 0¯Y -3.776E+0

Curve Fit: Y = aX + b
r = 0.9996
Y = 0.629E-2¯X + 3.296E-1
X = 0.311E + 1¯Y -4.320E+0

Curve Fit: Y = aX + b
r = 0.9994
Y = 3.614E-1¯X + 2.080E+0
X = 2.767E + 0¯Y -5.756E+0

Fig. 1. Emulsified aqueus standards calibration curves.

aqueous standard solutions and that obtained by using emulsion standard solutions. It can be seen that the concentrations of most elements are comparable, confirming the use of emulsions as an effective way to reduce or even eliminate of viscosity and making the direct introduction of such samples into ICP-MS instrument is possible.

CONCLUSIONS

Through this study, the main conclusion reached was that the method is simple, with low detection limits and acceptable precision. The comparison of emulsion methodology with acid digestion is a sign that it is accurate as the traditional methods but also easier and quicker.

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