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Direct injection high efficiency nebulizer-inductively coupled plasma mass spectrometry for analysis of petroleum samples

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Abstract

Direct injection high efficiency nebulizer (DIHEN)-inductively coupled plasma mass spectrometry (ICPMS) is investigated for analysis of petroleum samples dissolved in volatile organic solvents. To minimize solvent loading, the solution uptake rate is reduced to 10 $\mu\text{l}/\text{min}$, far less than the level (85 $\mu\text{l}/\text{min}$) commonly used for aqueous sample introduction with the DIHEN, and oxygen is added to the nebulizer gas flow and outer flow of the ICP. Factorial design is applied to investigate the effect of nebulizer tip position within the torch and the nebulizer and intermediate gas flow rates on the precision and the net signal intensity of the elements tested for multielemental analysis. Cluster analysis and principal component analysis are performed to distinguish the behavior of different isotopes, oxide species and doubly charged ions. The best operating conditions at a solution uptake rate of 10 $\mu\text{l}/\text{min}$ are: RF power=1500 W, nebulizer gas flow rate=0.10–0.12 l/min, intermediate gas flow rate=1.5 l/min and DIHEN tip position=3–4 mm below the top of the torch intermediate tube. Acceptable recoveries ($100 \pm 10\%$) and good precision (less than 3% relative standard deviation) are obtained for trace elemental analysis in organic matrices (a certified gas oil sample and a custom-made certified reference material) using flow injection analysis. Because of high blank levels, detection limits are 1–3 orders of magnitude higher for organic sample introduction than those acquired for aqueous solutions.

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1. Introduction

Inductively coupled plasma mass spectrometry (ICPMS) is a powerful technique for trace multielemental analysis of diverse samples dissolved in aqueous solutions [1]. However, the determination of trace elements in organic matrices (as in solvent extraction and the monitoring of wear metals in lubricating oils and other petroleum products) is often challenging, requiring procedures different

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from aqueous sample introduction. This is because the aerosol properties and the behavior of the inductively coupled plasma (ICP) with organic solvent introduction differ markedly from those encountered with aqueous solutions [1–9]. For instance, the ICP is usually operated at higher power levels and lower solution uptake rates with organic solvents compared to aqueous solutions because the decomposition of organic compounds in the plasma requires more energy [2,10].

Recently, a simple, relatively low-cost direct injection high efficiency nebulizer (DIHEN) was introduced in the marketplace for the direct nebulization of test solution into the plasma [11–26]. The DIHEN offers 100% analyte transport efficiency for the introduction of 1–100 $\mu\text{l}/\text{min}$ of test solutions into the ICP with no spray chamber or solution waste. In comparison to the direct injection nebulizer (DIN) [27–33], the DIHEN is less expensive, relatively easy to use, and requires no high-pressure pump for solution delivery. Direct injection of sample into the plasma with the DIHEN offers several benefits compared to the conventional nebulizer–spray chamber arrangement: (1) a low internal dead volume and thus rapid response times and reduced memory effects; (2) no volatile analyte lost in the spray chamber; (3) improved precision by eliminating noise sources attributed to the spray chamber; and (4) similar or improved detection limits and sensitivity when operated at microliters per minute compared to conventional nebulizer–spray chamber arrangement requiring milliliters per minute sample. However, the DIHEN introduces nearly four times more solvent (and analyte) [11], resulting in the deterioration of the plasma excitation and ionization properties and the increase in the spectral interferences, problems common to other direct injection nebulizers [27–33]. This attribute is particularly challenging when volatile organic solvents are introduced because of the plasma instability and the formation of carbon-based products on the nebulizer tip, torch confinement tube and sampling cone of the mass spectrometer interface [34]. To reduce or eliminate carbon formation, oxygen may be added to the nebulizer, intermediate or outer gas flows [31,33,35–42], but this addition must

be carefully controlled to prevent the degradation of the sampling cone and spectral selectivity.

This report is centered on investigation of the DIHEN for the introduction of samples dissolved in xylene using an argon–oxygen ICP to determine key elements important in petroleum industry. To facilitate multielemental analysis with DIHEN-ICPMS, the operating parameters were identified through factorial experiment design. A modified response surface design was used to obtain the best-compromised operating conditions for the plasma. To our knowledge, this report is the first account on the performance of the DIHEN for analysis of organic matrices.

2. Statistical methods used

2.1. Factorial design experiments

Several experiments are performed to identify the most influential factors, their ranges of influence, and factor interactions for organic solution introduction [43–46]. All factors are changed simultaneously at a limited number of factor levels. In one factorial design experiment, the screening design, two levels for each factor are used along with central points to check nonlinearities and estimate experimental error. In another factorial design, three levels for each factor are used to map the response surface. The drawback of this design is the large number of experiments that must be performed (3^n experiments compared to 2^n in the screening design; n is the number of parameters). Modified response surface designs, such as the central composite design and the Box–Behnken design, are more desirable to reduce the number of experiments [43]. In Box–Behnken design, as used in this work, the extreme factor levels are eliminated but the points are computed by approximation. This design is suitable for the investigation of the DIHEN for organic solvent introduction due to the delicacy of the nebulizer and the degradation possibility of the DIHEN tip due to excessive heating.

2.2. Principal component analysis and cluster analysis

Principal component analysis (PCA) and cluster analysis (CA) are unsupervised learning methods,

that is, they analyze data without the need for additional information about the measurements or numerical data. They are useful in finding structures or similarities (groups, class) in the data. PCA is a multivariate statistical technique that can be applied to a set of variables to reduce dimensionality, that is, to replace a large set of inter-correlated variables with a smaller set of independent variables [46–55]. The new variables, the principal components (PCs), are linear combinations of those in the original data set, but they are uncorrelated with each other. The first PC reflects the original variability as much as possible, while the second one embodies the remaining variability. The last few PCs correspond to random noise. To determine the main components in the PCA, a series of statistical and heuristic approaches can be used. In this study, eigenvalue-one criterion is applied where the average eigenvalue of all PCs is one and only those components with eigenvalues greater than one are considered important [43]. The application of PCA techniques in treating trace elemental analysis with ICPAES [45,52,53], and ICPMS [54,55] has been well documented.

Another multivariate statistical technique used in this study is CA that allows reducing the amount of data through categorization or grouping [43]. Clustering methods can be divided into two basic categories: hierarchical and partitional clustering. Each type utilizes different algorithms to find the clusters. Special rules are used to merge small clusters or split the large ones. The result is illustrated by a cluster tree or a dendrogram, which shows how the clusters are related to each other. A clustering of the data items into different groups may be obtained by cutting the dendrogram at a desired level. Hierarchical clustering is used in this study to reduce the amount of data and pattern recognition.

3. Experimental

3.1. Instrumentation

An Elan 6000 ICPMS system (Perkin–Elmer/Sciex Corporation, Norwalk, CT) was used under the operating conditions listed in Table 1. The nebulizer and outer gas flows consisted of Ar–O₂

mixtures. At the solution uptake rate of 10 $\mu\text{l}/\text{min}$ (see below), the amount of oxygen added to the cited flows (Table 1) was sufficient to provide stable plasma conditions for organic matrices and eliminate the formation of carbon-based products on the nebulizer tip, torch confinement tube and sampling cone of the mass spectrometer interface. Pure argon was used in this work with the DIHEN for the intermediate gas flow. In contrast, in conventional nebulization [35] oxygen is usually added to the intermediate gas flow to avoid carbon deposition on the torch intermediate tube. A maximum RF power of 1500 W was applied throughout this work to sustain stable plasma and avoid its degradation due to the addition of oxygen required to decompose the organic sample introduced directly into the plasma. All analytical data were collected under standard laboratory conditions, i.e. not in a clean-room environment.

3.2. Sample introduction systems

The DIHEN (Model DIHEN-170-AA, J.E. Meinhard Associates, Inc., Santa Ana, CA) was constructed from borosilicate glass, based on the nebulizer tip dimensions used earlier for a conventional HEN [11]. To minimize memory effects, the dead volume of the nebulizer was reduced to less than 15 μl by inserting a Teflon[®] capillary tubing (0.008 inch i.d. \times 0.016 inch o.d.; SB Fittings Assembly Kit no. 1-Micro, J.E. Meinhard Associates, Inc.) into the nebulizer to the point where the capillary tapers. This setup also allowed easy connection of the nebulizer to a micro flow injection valve. Argon flow rate was controlled by an external mass flow controller (Table 1). The output of the mass flow controller was connected to a gas proportioner (Model MFMR-0800-AA, E300/E200; Matheson Tri-Gas Inc.) where it was mixed with oxygen for delivery to the DIHEN.

A computer-actuated, metal-free, six port injection valve (Cetac Technologies, Inc., Omaha, NE) was used to position the sample plug between two air bubbles for delivery to the plasma (Fig. 1) using the timing sequence given in Table 1. Peak profiles were obtained by using Teflon[®] sample loops (Cetac Technologies, Inc.) for flow injection analysis. To reduce the dead volume, PEEK[®]

Table 1
Operating conditions for the DIHEN-ICPMS for organic solution introduction

ICPMS System	PE-Sciex Elan 6000	
RF power (W)	1500	
Nominal frequency (MHz)	40	
RF generator type	Free-running	
Induction coil circuitry	3-turn coil, PLASMALOK®	
Sampling depth (above load coil, mm)	11	
Sampler (orifice diameter, mm)	Nickel, 1.1	
Skimmer (orifice diameter, mm)	Nickel, 0.9	
Outer gas flow rate (l/min)	15 of Ar with 0.2% v/v O ₂ (30 ml/min of O ₂). A Matheson gas proportioner (Model MFMR-0800-AA; E800/E300) was used to mix gases.	
Intermediate gas flow rate (l/min)	1.5 (The gas flow was varied from 1.5 to 2.1 l/min for the factorial design experiments using a Matheson gas Flow meter; Model FM1050;E500)	
Sample introduction system	DIHEN (Model 170-AA, J.E. Meinhard Associates®, Inc.)	
DIHEN tip position (mm)	3 below intermediate tube (The position was varied from 3 to 8 mm for the factorial design experiments)	
Solution uptake rate (μl/min)	10	
Nebulizer gas flow rate (l/min)	0.12 of Ar with 37% v/v O ₂ (70 ml/min of O ₂). A Matheson gas proportioner (Model MFMR-0800-AA; E300/E200) was used to mix gases. Argon flow was varied from 0.10 to 0.15 l/min for the factorial design experiments.	
Solution flow mode	Continuous and FIA	
Timing parameters for flow injection analysis	Valve 1	Valve 2
Initial delay (s)	0	0
Load time (s)	60	155
Inject time (s)	285	190
Number of injections	1	1
Analysis time (min)	5.75	5.75
Data acquisition parameters	Peak hopping	
Scan mode	Peak hopping	
Points/mass	1	
Resolution (amu)	0.7	
Sweeps/reading	5	
Readings/replicate	3	
Replicates	5	
Dwell time/mass (ms)	50	
Integration time/mass (ms)	750	

tubing (0.010 inch i.d.×0.0625 inch o.d.; Upchurch Scientific Inc., Oak Harbor, WA) was used for all the connections on the flow injection valve, except for the DIHEN (see above). The carrier flow was ACS grade xylene (Fisher scientific, Fair Lawn, NJ) which was delivered (10 μl/min) to valve 1 using a syringe pump (Model KDS100, KD Scientific, New Hope, PA). With both valves in the *load* mode (Fig. 1a), this flow passed through the connecting tubing (PEEK®, 2-inch long) and valve 2 to the DIHEN. In this mode, the sample was pumped into a 20-μl sample

loop (Cetac Technologies) on valve 2 using a four-channel peristaltic pump (Rabbit, Rainin Instruments Co. Inc., Woburn, MA) and solvent-resistant pump tubing (0.015 inch i.d.; Astoria Pacific International, Clackamas, OR), while the other 20-μl loop on valve 1 was filled with air using the same peristaltic pump with an open-end peristaltic pump tubing (Fig. 1a). Once the air loop was full, that is, all the solvent from the previous run was drained out, valve 1 was switched to the *inject* mode, delivering the air bubble into valve 2 (Fig. 1b). This air bubble approached valve 2 and

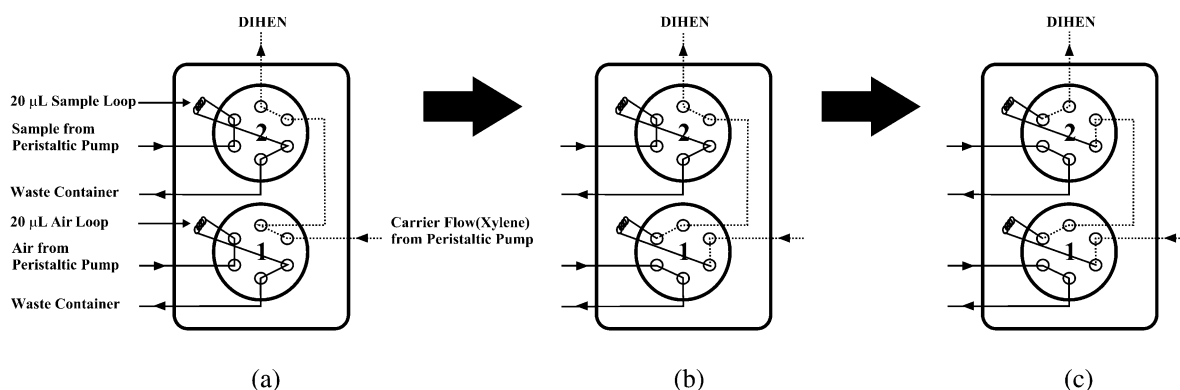


Fig. 1. Schematic diagram of the flow injection system used in this study: (a) Valve 1 and 2 are in the load mode. (b) Valve 1 is in the inject mode and valve 2 is in the load mode. (c) Valve 1 and 2 are in the inject mode.

moved toward the DIHEN as valve 2 was still in the load mode. When approximately half of this air bubble was pumped out of valve 2 (with the other half still in the connecting tubing), valve 2 switched to the *inject* mode (Fig. 1c). Consequently, the sample was positioned between two air bubbles. With this injection method, clean peaks with well-defined baselines were obtained and the memory effect was minimized.

3.3. Reagents

For optimization studies, three oil-based standards containing 50 µg/g of 21 elements, 100 µg/g of As and 100 µg/g of Hg (Conostan[®]

Division, Conoco Inc., Ponca City, OK) were diluted in xylene (Fisher Scientific) to a concentration of 200 ng/g. The elements measured in this study (Table 2) are of interest in petroleum industry, especially for environmental applications. To estimate the relative amount of doubly charged ions and oxide species; Ba⁺⁺ and BaO⁺ ions were also monitored.

For elemental analysis, the cited multi-element standard solutions were prepared at concentration levels of 5, 10, 25, 50, 75 and 100 ng/g to obtain external calibration curves and to conduct precision and detection limit studies. A certified gas oil sample (PDVSA INTEVEP, Caracas, Venezuela) was used for spike recovery experiments. To fur-

Table 2
Isotopes under study and potential isobaric interferences

Isotope	Natural abundance (%) ^a	Nominal mass (amu) ^a	Potential atomic isobars ^b	Potential molecular isobars ^c
⁵¹ V	99.8	50.9		HSO, ClO
⁶⁰ Ni	26.2	59.9		CaO
⁶⁹ Ba ⁺⁺	71.7	69.0		Ga, ClO ₂ , ArP, VO, Ce ⁺⁺ , La ⁺⁺
⁷⁵ As	100	74.9		ArCl, Sm ⁺⁺ , Eu ⁺⁺ , Nd ⁺⁺
¹⁰⁷ Ag	51.8	106.9		ZrO, YO
¹¹¹ Cd	12.8	110.9		MoO
¹³⁸ Ba	71.7	137.9	La, Ce	
¹⁵⁴ BaO	71.5	153.9	Sm, Gd	LaO, CeO
²⁰² Hg	29.9	202.0		WO
²⁰⁸ Pb	52.4	208.0		

^a From Ref. [56].

^b Potential atomic isobar of naturally occurring isotopes.

^c Partial list of potential molecular isobars.