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Single Nanoparticle Analysis of Asphaltene Solutions using ICP-QQQ

Agilent 8900 and ICP-MS MassHunter software module simplify spICP-MS analysis

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Introduction

Single Particle ICP-MS (spICP-MS) is increasingly being used to characterize the nanoparticle (NP) content of samples dispersed in an aqueous media (1−5). In several industries—including oil refining, petrochemicals, and semiconductor manufacturing—there is also interest in determining NPs in hydrocarbon matrices. In this study, we report a new method using triple quadrupole ICP-MS (ICP-QQQ) for the multi-element characterization of NPs in the heavy asphaltene fraction of petroleum (6). The method can be used to differentiate between metals present in NPs and the dissolved metal content. It will therefore extend the understanding of the role and form of metals present in crude oils and petroleum-based products. The method also has wider applicability to the characterization of NP populations in other hydrocarbon-based matrices, such as NMP, PGMEA, butyl acetate, and other organic solvents used in the semiconductor industry.

In spICP-MS analysis, the ICP-MS uses a fast time resolved acquisition mode to measure the signal generated by each NP as it passes through the plasma. The high sensitivity and low background noise of ICP-MS enables the signals generated from individual NPs to be distinguished, and these key performance characteristics are greatly enhanced with ICP-QQQ. The superior control of interferences achieved using tandem MS (MS/MS) operation means that ICP-QQQ is especially suitable for some of the elements of most interest in NP analysis, such as Si, Ti, Fe, S, and others.

The intensity of the NP signal peak is proportional to the size of the particle and the concentration (mass fraction) of the analyte element within the particle. The frequency of the individual NP signals is directly proportional to the number of NPs in the sample, allowing calculation of the NP size distribution, particle number, particle concentration, and dissolved metal concentration, all from a single ICP-MS measurement. Nanoparticle method setup, acquisition, calibration, and data reporting are simplified using the optional Single Nanoparticle Application Module of Agilent ICP-MS MassHunter software.

In this study, the spICP-MS acquisition mode of the Agilent 8900 ICP-QQQ was used to identify and characterize trace elements in asphaltenes—a complex class of high molecular weight hydrocarbons found in heavy oil fractions and bitumens. Asphaltenes are defined by their solubility class. They are soluble in aromatics such as benzene or toluene, but insoluble in lighter paraffins, such as *n*-pentane or *n*-heptane. Asphaltenes, together with waxes and resins, are of interest in petrochemical processing as they can deposit in equipment and pipelines leading to production problems. Asphaltenes also contain a high proportion of the metals in crude oil, including elements such as V and Ni, which act as catalyst poisons, affecting the oil refining process.

Iron- and Mo-based NPs were identified in the asphaltene samples. In contrast, V and Ni were found to be present mainly as dissolved metals, likely metal porphyrins and other organometallic species. Data is provided on the concentration and size distribution of Fe and Mo NPs in the asphaltene samples, and the levels of dissolved metals is also presented. The results highlight the potential of spICP-MS for the routine characterization of metal NPs—as well as dissolved metals— in asphaltenes, crude oils, petroleum-derived materials, and other organic sample-types.

Experimental

Reagents and samples

Trace metal grade purity chemicals were used throughout (*6*).

Three separate samples of asphaltene were obtained from different sources:

- Asphaltene A—a heavy Mexican crude oil (14° American Petroleum Institute, API).
- Asphaltene B—an asphaltenic deposit recovered from a submersible pump.
- Asphaltene C—an oxidized asphalt obtained from a commercial plant that produces specialty asphalts.

Sample preparation

The asphaltenes were extracted from the sample matrix using *n*-heptane at a sample/solvent ratio of 1/20. The blended crude oil/heptane was heated to 80 °C. After one hour, the undissolved asphaltenes were recovered by filtering the mixture through a 0.8 µ membrane filter.

Calibration standard preparation for total metals

Calibration standard solutions for direct analysis were prepared from Conostan (Quebec, Canada) S-21+K oil-based multi-element organometallic standard. The diluent comprised trace metal grade purity *o*-xylene (Fisher Scientific), a matrix modifier (made from mineral oil; Fisher Scientific), and a dispersant (Chevron Oronite). Scandium and yttrium were used as internal standards, spiked at 0.1 and 5 mg/kg, respectively.

Multiple calibration standards ranging from 1 to 1000 µg/kg for each of the target elements were prepared by weight from the 10 mg/kg Conostan multi-element standard and *o*-xylene diluent. The diluent solution was used as the blank for calibration.

Nanoparticle reference materials and sample preparation

A 60 nm silver (Ag) NP reference material (nanoComposix) was used to calculate the nebulizer efficiency. The Ag NP reference material and the three asphaltene samples were diluted to a particle concentration of between 40 and 1000 ng/g with *o*-xylene (via propylene glycol methyl ether acetate, PGMEA). The solutions were sonicated for 5 min to ensure sample homogeneity. Elemental response factors were determined by measuring elemental standards for each target analyte (10.0 µg/g) prepared with *o*-xylene.

Wet acid digestion for total metals

One to 5 g of each sample was heated on a hot plate at 100 °C for four hours with 1 to 2 mL of H_2SO_4 (93–98 % w/w). The solution was then subjected to an ashing sequence, as described in reference 6. Six mL HCl (34 to 37 % w/w) and 2 mL HNO_3 (67 to 70 % w/w) were added, before further heating on a hot plate at 100 °C for 1 hour. Before analysis, Sc was added as an internal standard (to give a final Sc concentration of 5 mg/kg) and the solution was brought to a final volume of 25 mL with Milli-Q water.

Instrumentation

An Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) equipped with the standard glass concentric nebulizer and Peltier-cooled quartz spray chamber was used. For the analysis of samples prepared in organic solvent (spICP-MS analysis and total metals determinations in the diluted asphaltene samples), an optional "organics" quartz torch with a 1 mm ID injector was used in place of the standard quartz torch, which has a 2.5 mm injector.

For the organic sample analyses, oxygen (20% in Ar) was added to the injector gas stream after the spray chamber. O_2 addition serves to decompose the carbon matrix thus avoiding carbon deposition on the interface cones. The more reactive plasma environment with O_2 addition requires the use of the more chemically resistant optional platinum-tipped sampling and skimmer cones.

The high sensitivity of the ICP-QQQ enabled the samples for NP analysis to be diluted by a factor between 1:2100 and 1:2700 in o-xylene. Applying a high dilution factor minimizes the risk of colloidal particles forming an agglomerate after nebulization. The dilution ensures that the NPs are dispersed in the solution so that each NP passes through the plasma separately from any other NPs. As a result, the signal peaks measured are each generated by a single particle event and not from multiple, overlapping particle signals.

Signal intensities for each NP target element were acquired in fast Time Resolved Analysis (fast TRA) mode using a dwell time of 0.1 ms (100 µs) per point, with no settling time between measurements. For Fe and Mo NPs, the signals were measured on-mass in MS/MS mode. For on-mass measurements, both quadrupoles (Q1 and Q2) were set to the target analyte ion mass of m/z 56 (for Fe) and m/z 95 (for Mo). Helium (He) cell gas was used in the 8900 ORS, to control the polyatomic interferences (mainly ArO on Fe at m/z 56). On-mass measurement with He cell gas was also used for the measurement of V and Ni (dissolved concentrations only—no NPs detected). ICP-QQQ operating conditions are given in Table 1.

Table 1. ICP-QQQ operating conditions.

Parameter	Value
RF power (W)	1600
Sampling depth (mm)	10
Carrier gas (L/min)	0.35
Spray chamber temperature (°C)	-5
Option gas (L/min) (Ar 80%, O_2 20%)	0.35
Dwell time (ms)	0.1
He cell gas flow rate (mL/min)	5.0

Simplified workflow

The optional Single Nanoparticle Application Module of the ICP-MS MassHunter software was used for NP data acquisition and analysis. The spICP-MS Method Wizard guides the user through the process of nanoparticle method setup, data acquisition, data analysis, and presentation of the NP results data.

Nebulization efficiency

Nebulization efficiency is the ratio of the amount of analyte (aerosol) delivered to the plasma as a proportion of the amount of analyte (solution) entering the nebulizer. In this work, the nebulization efficiency was determined using the Ag NP reference material of known (60 nm) particle size. The reference material was first dispersed in PGMEA, and then further diluted in o-xylene. Nebulization efficiency, calculated from the certified size of Ag NP reference material, was found to be 0.065 or 6.5%.

Results and Discussion

Nanoparticle size distributions

Nanoparticles containing Fe and Mo were detected in the asphaltene samples using the sp-ICP-MS method. By contrast, the signals for V and Ni were continuous, rather than the discrete signal pulses caused by the presence of clusters or particles of these elements. This finding indicates that V and Ni were most likely in the form of dissolved metal complexes. The TRA signal charts for Fe in sample B (Figure 1) and Mo in sample A (Figure 2) show the signal-intensity as a function of time. In spICP-MS, the peak area for each particle signal "plume" can be used to calculate the particle mass and therefore size.

According to the literature, the Fe NPs are most likely to be present as iron oxides (Fe_2O_3 or Fe_3O_4) (7) and pyrrhotite (FeS) (8). The Mo NPs are most likely present as molybdenite (MoS_2) (9), which is readily formed from oil-soluble Mo complexes present in heavy fractions from crude oils (10, 11).
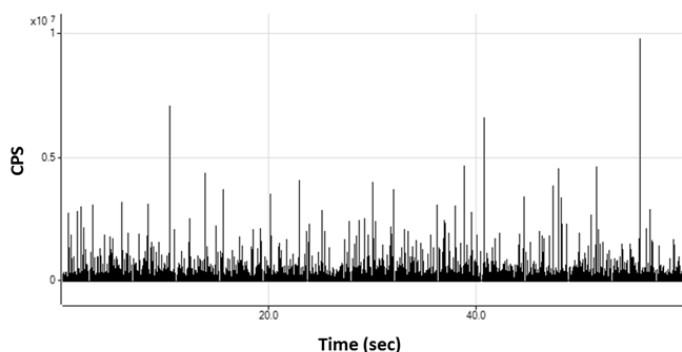

Figure 1. Asphaltene sample B: typical signals in counts per second (cps) for Fe (*m/z* 56) as a function of time.
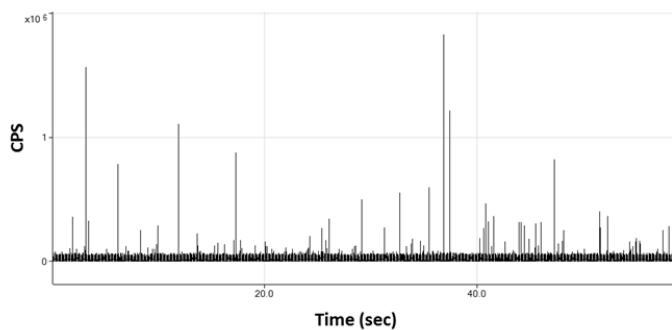

Figure 2. Asphaltene sample A: typical signals in counts per second (cps) for Mo (*m/z* 95) as a function of time.

The Fe and Mo NP size distribution plots for the three different asphaltene samples were calculated on the assumption that the Fe NPs were composed of Fe_2O_3, and the Mo NPs were composed of MoS_2. As shown in Figure 3, the average size of the Fe NPs varied among the samples. In contrast, the particle size distributions for Mo NPs are similar, with an average particle diameter in the range 70 to 80 nm (Figure 4).
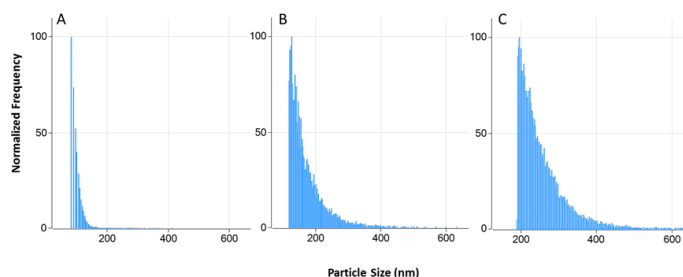

Figure 3. Comparison of size distributions for Fe NPs as Fe_2O_3 in the three asphaltene samples: A, B, and C. Modified with permission from J. Nelson et al., *Energy Fuels*, **2017**, 31 (11), 11971–11976. © 2017 American Chemical Society.

Figure 4. Comparison of size distributions for Mo NPs as MoS_2 in the three asphaltene samples: A, B, and C. Modified with permission from J. Nelson et al., *Energy Fuels*, **2017**, 31 (11), 11971–11976. © 2017 American Chemical Society.
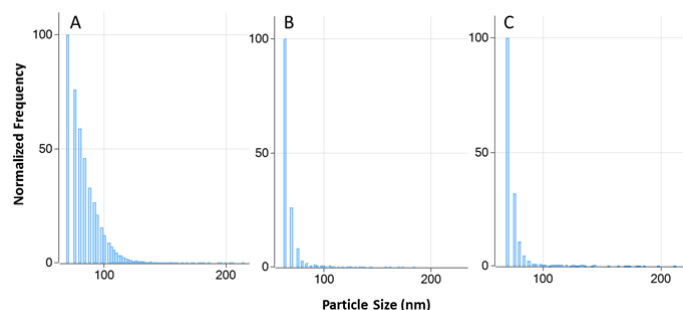
Concentration of the different forms of Fe and Mo

Uniquely, spICP-MS can distinguish between metal content that is contained in NPs (insoluble) and metal content that is dissolved in the sample matrix. The relative NP and soluble concentration data for Fe and Mo in the three asphaltene samples is given in Table 2. The data indicates that there was some variation in the distribution of metals among the asphaltene samples. In samples A and B, Fe was mostly present as NPs (76 and 91 wt. %, respectively), while in asphaltene sample C, less than half the Fe content was present as NPs. By contrast, Mo was almost all present as soluble forms (between 60 and 99 wt. %) in all three asphaltene samples, as shown in Table 2.

Total concentration of Fe and Mo

The total concentrations of Fe and Mo from the spICP-MS analysis (sum of the particle concentration and the dissolved concentration) were compared to the total metal concentrations measured by direct dilution and wet acid digestion. The results, which are given in Table 2, indicate that there was some variation between the three separate results for total concentrations of Fe and Mo. The spICP-MS and acid digestion approaches gave similar results for total Fe in all three samples, with the direct dilution results being consistently lower. This low bias for Fe present as particles in samples prepared and introduced using direct dilution has been reported in the literature (12). A study using Laser Ablation-ICP-MS (13) has also shown that large particles are not completely vaporized and ionized in the plasma. This finding could account for the low recovery observed for Fe in the direct analysis of the diluted samples. The difference compared to the spICP-MS total concentration may be due to the way the relatively large particles in these asphaltene samples are calibrated in spICP-MS vs the effect of incomplete dissociation and ionization of these larger particles measured by direct dilution.

The concentrations for Mo following direct dilution compare well with those obtained using wet acid digestion. For sample C, the total concentration found using spICP-MS also agrees well. But for the other two samples, the spICP-MS results do not tally with the total Mo concentrations found by the dilution and digestion methods. Total Mo by spICP-MS was found to be lower in Sample A and higher in Sample B, compared to total Mo determined by the other two approaches. Further studies are underway to investigate the discrepancies in the total concentration values for Mo calculated using the spICP-MS method compared with direct dilution and wet acid digestion.

Conclusions

Single particle-ICP-MS is becoming a widely used and well-established technique for the characterization of NPs in aqueous-based solutions. In this study, we show the potential for the spICP-MS methodology to be applied to complex hydrocarbon-based matrices of interest in petroleum refining and other industries.

The Agilent 8900 ICP-QQQ is especially suited to spICP-MS analysis because of its high sensitivity, low background, and unmatched control of spectral interferences. Setup and analysis for NP applications is facilitated by the optional Single Nanoparticle Application Module for ICP-MS MassHunter software.

Iron and molybdenum NPs were determined in three asphaltene samples from different sources associated with oil refining and petroleum-related product processing. No nickel or vanadium-containing NPs were detected in the heavy petroleum fractions suggesting that these elements are more likely to form dissolved organometallic complexes, such as porphyrins. This spICP-MS method is also able to differentiate between metal-containing NPs and dissolved metals.

Further work is in progress to expand the spICP-MS method for the routine characterization of metals in petroleum-derived samples, as well as in other hydrocarbon-based samples.

Table 2. Concentrations of Fe and Mo present in NPs and dissolved in the matrix (soluble), calculated using spICP-MS, compared to total concentrations determined by direct ICP-MS analysis following two different preparation techniques.

Asphaltene samples	Iron concentration, mg/kg					Molybdenum concentration, mg/kg				
	NPs	Soluble	Total, spICP-MS	Total, direct dilution	Total, wet acid digestion	NPs	Soluble	Total, spICP-MS	Total, direct dilution	Total, wet acid digestion
A	54.0 (76%)	17.0	71.0	39.5	68.0	3.48	5.33 (60%)	8.81	39.7	40.4
B	173 (91%)	17.0	190	84.4	221	0.04	3.23 (99%)	3.27	0.78	0.52
C	457 (47%)	508	965	420	750	0.07	6.33 (99%)	6.40	5.89	6.22

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