APPLICATION NOTE

ICP – Mass Spectrometry

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Determination of Elements at Sub-ppb Concentrations in Naphtha Mixtures Using the NexION 300 ICP-MS

Abstract

The analysis of organic solvents by ICP-MS is challenging due to their high carbon content and volatility. Naphthas are an important class of organic liquids produced in the petrochemical industry, byproducts of the crude-oil refining process. Because they are organic based and have a variety of compositions, naphthas present a special challenge for ICP-MS analysis: the carbon causes polyatomic interferences and can clog interface cones, and the varying volatility means that it is difficult to use a single set of calibration standards for a variety of different naphtha compounds. Using the NexION™ 300 ICP-MS, several naphtha compounds (ranging from light to heavy naphthas) were successfully analyzed using a single set of calibration standards and operating conditions, demonstrating the accuracy and stability of the method.

Introduction

Analysis of trace metals in organic matrices, such as naphtha, by ICP-MS has historically been very difficult. ICP-MS technology has the sensitivity and multi-element capabilities desired, but there are many hurdles that must be overcome. Volatile organic liquids pose a challenge by overloading the plasma with vapors from the solvent, which can reduce sensitivities, destabilize, or even extinguish the plasma. The extremely high carbon content in solvents results in deposition of carbon particles or soot on the sampler cone, occluding the orifice and causing signal drift. The excessive carbon also creates interferences from carbon-based polyatomic species such as $^{12}C^{14}NH^+$ and $^{13}C^{14}N^+$ which interfere with $^{27}Al^+$ and $^{40}Ar^{12}C^+$ which interferes with $^{52}Cr^+$. Each of these issues must be addressed for successful application of ICP-MS to the analysis of naphthas.

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There are a number of measures that can be implemented to overcome the issues mentioned above. Wet ashing organic samples decomposes the organic matrix and ultimately solubilizes the elements in an aqueous matrix. However, this procedure is time intensive and involves significant manipulation of the samples, which provides opportunities for contamination and element loss. Direct analysis can be a much more efficient and accurate technique when the matrix issues are addressed. The vapor pressure of the solvents can be lowered by chilling the spray chamber and hence reducing the vapor loading on the plasma. The carbon deposition can be eliminated by the addition of oxygen into the nebulizer stream. The formation of interfering polyatomics can be addressed with the use of reaction gases in a Dynamic Reaction Cell™ (DRC™).

Naphtha is a relatively generic term referring to a broad range of middle-distillate hydrocarbon mixtures typically produced by petroleum refineries from crude oil. Naphthas represent that fraction of crude oil that falls between the light gases and the heavier kerosene and may have carbon chains ranging from C_5 to C_{13} and a boiling-point range from as low as 27 °C to as high as 260 °C. There are many types of naphthas with numerous common and brand names that can be quite confusing. In general, naphthas can be differentiated by their hydrocarbon fractions; the most commonly referred-to fractions include paraffins (a.k.a. normal alkanes), isoparaffins (a.k.a. branched alkanes), olefins (a.k.a. alkenes), naphthenes (a.k.a. cyclic alkanes), and aromatics. Lighter naphthas tend to contain high percentages of paraffins, whereas heavier naphthas may contain high percentages of naphthenes and aromatics.

Analysis of naphthas for trace elements is important for a number of reasons. Naphthas are used as fuel in combustion engines where elements such as calcium, magnesium, sodium, and potassium can form hard deposits and create excessive wear on the engine components. Naphthas are also used as feedstock in catalytic reformers which rearrange the hydrocarbon molecules as well as break some of the molecules into smaller molecules to produce high-octane components of gasoline. In addition, naphthas are used as feedstock for steam reformers and steam crackers for the production of hydrogen. Elements including nickel, vanadium, and mercury have been shown to poison the catalyst or cause corrosion in these systems. Some elements are of environmental concern. Emission from combustion engines and the refining process can release heavy metals into the atmosphere. As such, monitoring of elements such as arsenic, mercury, and lead is important.

This work demonstrates the ability of the PerkinElmer® NexION 300 ICP-MS to successfully analyze several naphtha compounds (ranging from light to heavy naphthas) under a single set of instrumental conditions. Carbon-based interferences are removed, providing accurate results, and stability is demonstrated through repeated analysis of a single sample over time. This initial work was performed with a limited number of elements, but will be extended in the future.

Experimental

Sample Preparation

For this study, three different naphthas were used. Two of the naphthas were similar and represented the light naphthas: petroleum ether (Burdick & Jackson®) and ligroin (Aldrich®), with boiling-point ranges between 35-60 °C and 60-80 °C, respectively. The third naphtha, Stoddard solvent (EMD Chemicals®), is a heavier naphtha with a boiling-point range of 154-202 °C. Such a wide array of hydrocarbon composition and boiling-point ranges can pose a significant challenge when trying to analyze such an assortment of naphthas in the same run. Two significant issues that need to be addressed are creating adequate sample-introduction conditions to effectively handle the range of naphthas and calibration.

Because of the complications associated with analyzing naphthas on ICP-MS, Method of Standard Additions (MSA) is often used. With MSA, each and every sample is spiked with varying concentrations of target elements to create a calibration within the sample matrix. However, this is a tedious and time-consuming process. The use of an external calibration would be much more efficient but typically does not work well with such a challenging matrix. Two procedures were implemented to address the matrix effects: chilling of the spray chamber and dilution of the naphthas in another solvent.

The diluent was semiconductor-grade xylene (mixed isomers), which was also used as the rinse. Xylene was used as a diluent as it is in the same carbon chain group as naphthas (C_8), is readily miscible with naphthas and the calibration solutions, and has a similar boiling-point range (137-144 °C), at least to the heavier naphtha, Stoddard solvent. The use of semiconductor-grade solvent ensured that the naphtha samples would not be contaminated with elements of interest, as well as ensuring a clean blank. Because commercial calibration standards are not currently available in a naphtha or xylene matrix, organometallic standards from Conostan® were used following dilution with the xylene. Conostan®'s oil analysis standards, both mixed and single-element, ranging in concentration from 100 to 1000 µg/g in 75 centistoke base mineral oil, were diluted in the xylene. Because of the high stock concentrations, the dilution factors needed to produce the working calibration standards was such that the working-standards matrix was more than 99.99% xylene which, as previously stated, is relatively similar to naphthas. The external calibration curves were comprised of standards at 0.2, 1, and 10 µg/L. The naphtha samples themselves were diluted 1:10 in the xylene. This dilution factor was sufficient to homogenize the matrix variations while still allowing for sub-ppb detection limits. All samples and standards were spiked with internal standards (Li, Y, In, and Bi) at 10 µg/L.

Instrumental Parameters

A NexION 300D ICP-MS was used to perform all analyses; the instrumental conditions are listed in Table 1. Carbon-based interferences include $^{12}C^{12}C^+$, $^{12}C^{14}NH^+$, $^{40}Ar^{12}C^+$, and $^{40}Ar^{16}O^+$ on $^{24}Mg^+$, $^{27}Al^+$, $^{52}Cr^+$, and $^{56}Fe^+$, respectively. Ammonia was used to remove these interferences; Table 2 shows the cell conditions used.

Table 1. **NexION 300D ICP-MS Instrumental Conditions.**

Sample Uptake Rate	200 µL/min
Peristaltic Pump Tubing	Viton®
Nebulizer	Glass concentric
Spray Chamber	PC^3 LT with baffled glass cyclonic
Spray Chamber Temperature	-20 °C
O_2 Flow	25 mL/min
Injector	0.85 mm quartz
RF Power	1600 W
Dwell Time	50 ms
Sweeps/Reading	20
Replicates	2
Modes	DRC (NH_3) and Standard
Sample Run Time	1.7 min/sample

Table 2. **Reaction Cell Conditions.**

Element	Cell Gas	Gas Flow (mL/min)	RPq
Al 27	NH_3	0.6	0.60
Cr 52	NH_3	0.6	0.65
Fe 56	NH_3	0.6	0.45

Because of the high organic content and volatility of the samples, several modifications were made to the standard sample-introduction system. The sample-uptake rate was 200 µL/min, using orange/yellow Viton® pump tubing and a peristaltic pump speed of 10 rpm. The spray chamber was drained with black/black Viton® tubing.

Sample was aspirated through a glass Meinhard® nebulizer into a PC^3-LT Peltier-cooled glass spray chamber (Elemental Scientific, Inc., Omaha, NE, USA) at -20 °C to eliminate the solvent vapor loading on the plasma by lowering the vapor pressure of the naphthas. Chilling the spray chamber also helps to stabilize the plasma conditions while analyzing the various naphthas. Conditions at 2 °C and -5 °C were evaluated on the ESI PC^3, but it was only with the ESI PC^3LT at -20 °C that the naphthas generated consistent results, as determined by recoveries of internal standards. Even at -20 °C, when the naphthas were run without dilution, there were significant differences in the plasma conditions (e.g., plasma flicker), internal standard recoveries, and signal suppression. However, with the 1:10 dilution in xylene, there were no noticeable differences in the plasma conditions and internal standard recoveries were consistent.

Introduction of oxygen into the nebulizer stream can be used to effectively prevent the buildup of non-ionized carbon on the interface cones, primarily the sampler cone. The oxygen flow was controlled with a mass flow controller and was introduced via a port in the outlet of the spray chamber. The correct oxygen flow was determined by increasing the flow until the Swann bands disappeared in the plasma, as viewed through the NexION's plasma-view window (Figure 1). Delivering the optimum flow of oxygen is important as too little will allow the formation of carbon on the cones and too much can destabilize the plasma as well as speed up the devitrification of the quartz torch and create a more corrosive environment for the cones. An additional effect of excess oxygen is that the formation of oxides is increased, particularly for easily oxidized elements such as Hg. This may result in significantly reduced intensities as the observed *m/z* ratio is shifted to that of the oxides. The amount of oxygen needed is, in part, dependent on the carbon-chain length – that is, the longer the carbon-chain length, the more oxygen is needed. The plasma-view window allows for the accurate determination of just the right amount of oxygen.

To further reduce carbon-loading on the plasma, a 0.85 mm injector was used. Platinum cones were chosen to withstand the corrosive environment created by oxygen addition.

Figure 1. Plasma view on the NexION 300 ICP-MS.

Results and Discussion

Since no commercial standard reference materials are available for naphtha, the efficacy of the method conditions was demonstrated by spiking each of the three naphthas with target elements at low concentrations (0.2 – 1.0 µg/L), after 10x dilution with xylene. The method detection limits in the naphthas were determined by measuring each spiked sample seven times and multiplying the standard deviation by 3.14 (the t-value for 6 degrees of freedom). Table 3 shows the DLs for the three samples. Tables 4-6 (Pages 4-5) show 5 µg/L spike-recovery data for all three samples.

Table 3. **Detection Limits in Naphtha Solvents (ng/g).**

Element	Mass	Stoddard Solvent	Ligroin	Petroleum Ether
V	51	0.200	0.015	0.012
Mn	55	0.038	0.031	0.017
Ni	58	0.062	0.017	0.015
Cu	63	0.080	0.015	0.017
Se	82	0.150	0.051	0.043
Cd	114	0.036	0.031	0.017
Sn	120	0.084	0.025	0.012
Ba	138	0.067	0.022	0.018
Hg	202	0.170	0.022	0.015
Pb	208	0.044	0.017	0.017
Al*	27	0.017	0.048	0.025
Cr*	52	0.030	0.040	0.012
Fe*	56	0.025	0.024	0.017

** = DRC mode*

Table 4. **Spike Recoveries in Petroleum Ether.**

Element	Mass	Solvent (µg/L)	Spike (µg/L)	%Recovery
V	51	0.00	6.45	129
Mn	55	0.22	5.15	98.6
Ni	58	0.11	5.24	103
Cu	63	0.05	4.76	94.2
Se	82	0.00	5.41	108
Cd	114	0.10	5.35	105
Sn	120	0.01	5.63	112
Ba	138	0.01	4.74	94.6
Hg	202	0.02	5.28	105
Pb	208	0.03	4.81	95.6
Al*	27	0.21	6.15	123
Cr*	52	0.00	6.15	123
Fe*	56	0.05	6.54	130

** = DRC mode*

Table 5. **Spike Recoveries in Ligroin.**

Element	Mass	Solvent (µg/L)	Spike (µg/L)	%Recovery
V	51	0.01	6.18	123
Mn	55	0.28	5.16	97.6
Ni	58	0.20	5.30	102
Cu	63	0.11	5.00	97.8
Se	82	0.07	5.40	106
Cd	114	0.21	5.16	99.0
Sn	120	0.08	5.36	106
Ba	138	0.02	4.82	96.0
Hg	202	0.06	5.00	98.8
Pb	208	0.03	4.90	97.4
Al*	27	0.24	5.24	100
Cr*	52	0.01	5.56	111
Fe*	56	0.08	5.84	115

**= DRC mode*

Table 6. **Spike Recoveries in Stoddard Solvent.**

Element	Mass	Solvent (µg/L)	Spike (µg/L)	%Recovery
V	51	0.01	5.06	101
Mn	55	0.06	4.97	98.2
Ni	58	0.02	4.83	96.2
Cu	63	0.03	4.64	92.2
Se	82	0.06	4.66	92.0
Cd	114	0.01	5.07	101
Sn	120	0.06	4.91	97.0
Ba	138	0.01	4.82	96.2
Hg	202	0.02	4.87	97.0
Pb	208	0.01	4.85	96.8
Al*	27	0.07	4.82	95.0
Cr*	52	0.00	4.86	97.2
Fe*	56	0.01	4.87	97.2

** = DRC mode*

The stability of the method was demonstrated by monitoring recoveries of the internal standards over time. Each of the naphthas, diluted 1:10 in xylene, was analyzed repeatedly over time, using xylene as the rinse between replicate measurements. Long-term stability is shown in Figure 2 (Page 6), with the results of normalized intensities from petroleum ether, a light naphtha, over a 2.5-hour period. Much longer stability is possible.

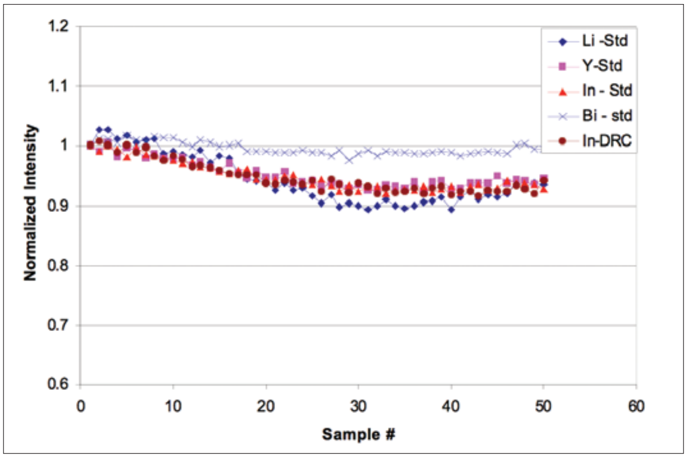

Figure 2. 2.5-hour stability of petroleum ether.

Conclusions

This work has demonstrated that the PerkinElmer NexION 300 ICP-MS is an ideal instrument for trace-level metals analysis of complex and highly variable naphtha solvents. Robust, high-power plasma conditions, along with a chilled spray chamber, are able to easily handle the solvent matrix and provide excellent stability. The plasma-view window allows for simple determination of the optimum oxygen-addition flow to prevent carbon deposits. The combined Triple Cone Interface and Quadrupole Ion Deflector create a tightly focused ion beam with unrivaled reduction of neutral species, photons, and particulate deposits. Polyatomic species, particularly those based on carbon, are all but eliminated with the use of the Universal Cell in DRC mode. With this combination of features, excellent detection limits and stability can be achieved with minimal sample handling. Under one set of operating conditions, complex organic liquids such as naphtha solvents, can be analyzed. Future work will focus on extending the number of elements analyzed in naphthas.

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