

Quadrupole ICP-MS for the Direct Analysis of Ammonia Solution and Organic Solvents

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Overview

Purpose: Direct organic solvent and ammonia solution analysis by ICP-MS is notoriously difficult due to overload of the plasma, chemical incompatibility and contamination issues. Advanced sample handling techniques that overcome these issues were evaluated.

Methods: A dual syringe pump and sampling valve introduction system coupled to Quadrupole ICP-MS (ICP-Q-MS) is presented.

Results: The figures of merit for the direct analysis of ammonia solution and organic solvents show minimal contamination, stable long term analysis and improved limits of detection (LODs).

Introduction

Routine, auto sampler based trace element analysis of organic solvents by ICP-MS has historically been considered difficult due to a range of potential problems. Sample introduction of organic solvents using a peristaltic pump is complicated by possible chemical incompatibility while any tubing found to be chemically resistant can also be a significant source of contamination.

For this reason, sample introduction based around self-aspiration is often the only choice available to the analyst. When using self-aspiration however, differing viscosities and specific gravities may also lead to unreliable uptake times when analyzing different solvents in an analytical run. The high volatility of many organic solvents further complicates the analysis. Another difficult application is the direct analysis of undiluted ammonia solution.

To overcome problems, dilution or other sample pre-treatment is often employed, but this introduces a time-consuming step in the analytical protocol and increases the potential for contamination.

This poster highlights the efficient, accurate and contamination-free analysis of various volatile organic solvents and ammonia solution using the Thermo Scientific XSERIES 2 quadrupole ICP-MS from Thermo Fisher Scientific coupled with the advanced Dual Syringe Pump SC4-FAST sample introduction system from Elemental Scientific, Inc. (ESI) (Figure 1).

The ESI FAST system is based around a vacuum loaded injection valve and sample delivery by syringe pumps (Figure 2), dramatically facilitating the analysis of organic solvents and ammonia solution.

Methods

The XSERIES 2™ ICP-MS was configured with a Syringe Pump SC4-FAST system from ESI (Elemental Scientific, Inc., Omaha, NE, USA).

The schematic in Figure 3 outlines the principle of the FAST system that uses syringe pumps to load samples onto and inject samples from a six-port switching valve. The advantages of this system for the routine analysis of organic solvents can be summarized as:

- Syringe pumps reliably deliver organic solvents of different physical properties, thus eliminating sample introduction with peristaltic pumps
- The specially designed syringe pumps smoothly deliver high volatility organic solvents at low flow rates (from $5 \mu\text{L}/\text{min}$ to $50 \mu\text{L}/\text{min}$) avoiding any overloading of the ICP
- All surfaces that the sample comes into contact with are made from PFA, facilitating an inert, non-contaminating sample introduction
- The valve system reduces uptake and washout times dramatically for improved sample throughput

Instrumental parameters for the combined SC-FAST XSERIES 2 System are shown in Table 1.

FIGURE 1. Thermo Scientific XSERIES 2 ICP-MS and ESI syringe pump SC4-FAST system.



FIGURE 2. Close-up of the syringe pump and switching valve assembly.

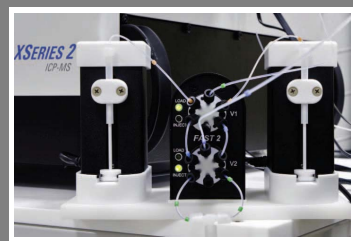


FIGURE 3. Dual Syringe SC FAST automated introduction system.

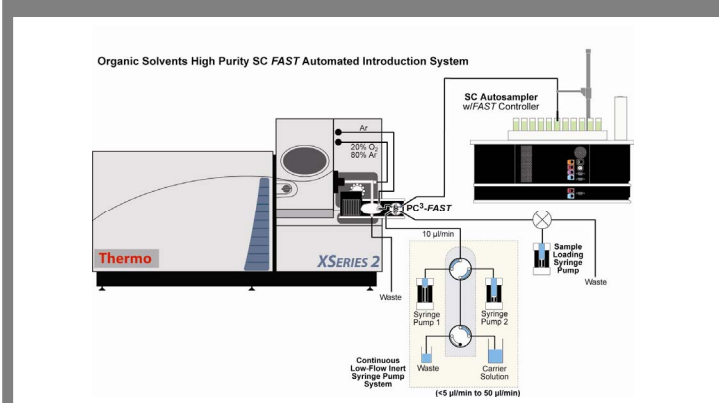


TABLE 1. Instrument operating parameters.

| Dual Syringe FAST System | | |
|--------------------------|--|--|
| Sample | Naphtha, Hexane | Ammonia Solution |
| Carrier | Hexane | Ammonia Solution |
| Loop Volume | 250 $\mu\text{L}/\text{min}$ | 250 $\mu\text{L}/\text{min}$ |
| Carrier Flow Rate | 5 $\mu\text{L}/\text{min}$ | 20 $\mu\text{L}/\text{min}$ |
| ICP-MS | | |
| Nebulizer | Micro flow PFA | Micro flow PFA |
| Interface | Pt tipped sample cone and Xt skimmer cone | Pt tipped sample cone and Xt skimmer cone |
| Spray chamber | Cyclonic, peltier cooled to -5 °C | Cyclonic, peltier cooled to 2 °C |
| Torch | Pt injector Demountable injector with Plasmascreen | Pt injector Demountable injector with Plasmascreen |
| Additional gas | Pure Oxygen 40 mL/min | 0.71 mL/min |
| Nebulizer gas | 0.75 mL/min | 0.71 mL/min |
| Forward power | 1500 W | 1400 W |
| Collision gas | 8% H ₂ gas in He at 7.5 mL/min | 8% H ₂ gas in He at 7.5 mL/min |

Direct Trace Metal Analysis of Organic Solvents

Naphtha

In the petrochemical industry, the determination of trace metals in naphtha is important as some elements can lead to difficulties in subsequent processing as well as contamination of end products. Non-volatile elements such as Pb are easily removed during refinement but Hg, due to its volatility is more problematic and its analysis demands increased sensitivity and accuracy. As Hg acts as a poison to the precious metal based catalysts, the production of low Hg containing naphtha is therefore of increased focus. The multi element and single element Hg standards used in this work were sourced from CONOSTAN® (USA, www.conostan.com) (Figure 4).

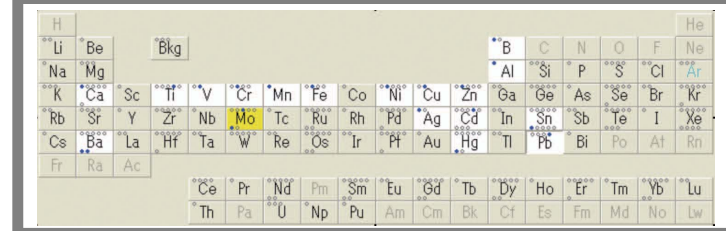
Naphtha from Fisher Scientific Inc. (Reference N/0050/PB17) was used in all analyses.

FIGURE 4. Conostan® single and multi-element oil analysis standards.



The XSERIES 2's powerful Collision Cell Technology (CCT) with its use of a single H₂/He cell gas mixture was used for the analysis of Ca, Cr and Fe in order to remove spectral interferences resulting from the high carbon content in the sample. All other elements were analyzed in standard mode.

FIGURE 5. List of analytes determined in the naphtha sample.



For quantification of trace elements in naphtha, fully quantitative calibrations were performed and ⁹⁹Mo was used as internal standard. Figure 6 shows the fully quantitative calibration for Hg in naphtha.

FIGURE 6. Fully quantitative calibration for Hg in naphtha.

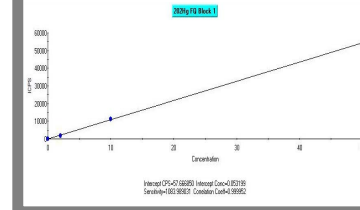


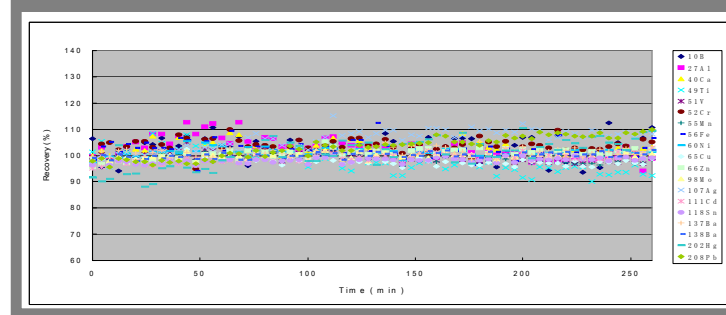
TABLE 2. Mercury memory test results.

| Sample list | Run Times | ICPS at ²⁰² Hg |
|------------------|------------------|---------------------------|
| Naphtha | 10/29/2008 13.40 | 58 |
| Naphtha Hg 2ppb | 10/29/2008 13.43 | 1869 |
| Naphtha Hg 10ppb | 10/29/2008 13.47 | 11152 |
| Naphtha Hg 50ppb | 10/29/2008 13.50 | 54221 |
| Naphtha | 10/29/2008 13.52 | 311 |
| Naphtha | 10/29/2008 13.55 | 134 |
| Naphtha | 10/29/2008 13.57 | 96 |

Table 2 shows that seven minutes after the analysis of the 50 ppb Hg naphtha standard, the Hg background recorded in a pure naphtha sample had dropped down to a background subtracted equivalent concentration of <math>< 50 \text{ ppt}</math> (less than 0.1% washout).

In order to test the stability of the analysis, a sample of naphtha spiked with 10 ppb of a range of elements was repeatedly analyzed over a 4-hour period. Normalized results illustrate the recovery of the 10 ppb spike (Figure 7).

FIGURE 7. Recoveries for 10 ppb spiked Naphtha sample over 250 minutes (200 runs).



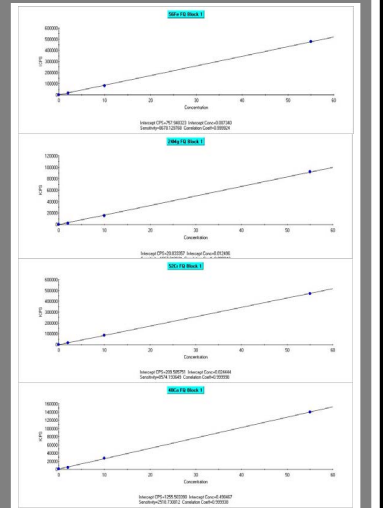
Hexane

Hexane is difficult to analyze directly by ICP-MS. With the Dual Syringe SC-FAST system, however, direct analysis of this challenging solvent was possible. Fully quantitative calibration curves were generated for a number of trace elements in hexane (Fisher Scientific PN H303-1). The ICP-MS acquisition parameters used for naphtha were applied here. Figure 8 shows fully quantitative calibration curves of ²⁴Mg, ⁴⁰Ca, ⁵²Cr and ⁵⁶Fe. BECs and LODs were calculated for each analyte (Table 3).

TABLE 3. LOD and BEC data for trace elements in hexane. All values are shown in units of ppb.

| Element | LOD (3 σ) | BEC |
|-------------------|-------------------|--------|
| ¹⁰ B | 0.491 | 4.69 |
| ²⁴ Mg | 0.002 | 0.012 |
| ³⁹ K | 0.127 | 4.66 |
| ⁴⁰ Ca | 0.032 | 0.050 |
| ⁵¹ V | 0.097 | 0.220 |
| ⁵² Cr | 0.002 | 0.024 |
| ⁵⁴ Mn | 0.064 | 0.073 |
| ⁵⁶ Fe | 0.012 | 0.087 |
| ⁵⁷ Ni | 0.068 | 0.095 |
| ⁶³ Cu | 0.030 | 0.070 |
| ⁶⁶ Zn | 0.059 | 0.139 |
| ⁸⁸ Mo | 0.002 | 0.002 |
| ¹⁰⁷ Ag | 0.003 | 0.003 |
| ¹¹¹ Cd | 0.003 | 0.001 |
| ¹¹³ Sn | 0.001 | 0.004 |
| ¹³⁵ Ba | 0.001 | 0.0004 |
| ²⁰⁸ Pb | 0.001 | 0.0004 |

FIGURE 8. Hexane fully quantitative calibration results.



Direct Trace Metal Analysis of Ammonia Solution

Direct aspiration of undiluted ammonia is highly problematic for ICP; dilution or condensation techniques are commonly employed. With the SC-FAST and dual syringe pump, direct ammonia analysis is possible. The multi-element standard used in this work was sourced from SPEX (http://www.spexcsp.com/). The ammonia solution was purchased from Fisher Scientific (PN A/3365/07). A number of analytes (listed in Table 3) were determined with CCT or in standard mode. Example fully quantitative calibration curves are presented in Figure 9. Limits of detection for each analyte are shown in Table 4.

FIGURE 9. Ammonia solution fully quantitative calibration results.

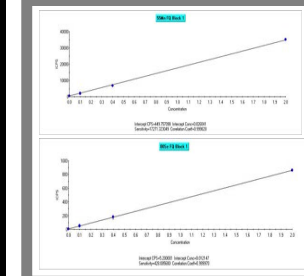


TABLE 4. LOD data for trace elements in ammonia solution. All values are shown in units of ppb.

| Element | LOD(3 σ) | Element | LOD(3 σ) |
|------------------|------------------|-------------------|------------------|
| ⁷ Li | 0.001 | ⁷¹ Ga | 0.001 |
| ²³ Na | 0.071 | ⁷⁵ As | 0.002 |
| ²⁴ Mg | 0.009 | ⁸⁶ Se | 0.013 |
| ²⁷ Al | 0.011 | ⁸⁵ Rb | 0.000 |
| ³⁹ K | 0.073 | ⁸⁸ Sr | 0.002 |
| ⁵¹ V | 0.001 | ¹⁰⁷ Ag | 0.002 |
| ⁵² Cr | 0.002 | ¹¹¹ Cd | 0.001 |
| ⁵⁴ Mn | 0.002 | ¹¹³ In | 0.003 |
| ⁵⁶ Fe | 0.005 | ¹³⁷ Ba | 0.008 |
| ⁵⁹ Co | 0.004 | ²⁰⁵ Tl | 0.001 |
| ⁶⁰ Ni | 0.010 | ²⁰⁸ Pb | 0.004 |
| ⁶³ Cu | 0.005 | ²⁰⁹ Bi | 0.003 |
| ⁶⁶ Zn | 0.023 | ²²⁸ Tl | 0.002 |

Conclusions

The combination of the Thermo Scientific XSERIES 2 and the ESI Dual Syringe SC-FAST sample introduction system provides a valuable routine tool for the direct trace metal analysis of highly volatile organic solvents such as naphtha, hexane and ammonia solution. The SC-FAST sample introduction system provides a rapid, contamination-free sampling technology with full automation for routine analysis. Through implementation of 3rd Generation CCT technology, the XSERIES 2 provides a sensitive and interference-free instrumental solution for the trace elemental determination even in such demanding matrices.

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