Part I: Dealing with High Matrix Samples

Analysis of Trade Waste Effluent by ICP-MS
10/01/2015

Speakers:
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Brian Walker – Sembcorp Industries
Outline for Today’s Talk

- Overview of the U.S. Clean Water Act
- EPA wastewater regulations
  - NPDES program
  - The pretreatment Program
- Analytical methods
  - Approved methods
  - Specific methods—mercury measurement
- EU wastewater regulations
- Resources
U.S. Wastewater Regulations

• The Clean Water Act (CWA)
  • Federal Water Pollution Control Act (1948), then became
  • The Clean Water Act (1972)
  • “The CWA made it unlawful to discharge any pollutant from a point source into navigable waters, unless a permit was obtained.”
  • “EPA's National Pollutant Discharge Elimination System (NPDES) permit program controls discharges”
    • Resident homes do not need permit for their sewage disposal (linked to municipal pipes)
    • Municipal and industrial disposal directly goes to surface water and requires a permit

Source: EPA website
http://www2.epa.gov/laws-regulations/summary-clean-water-act
The NPDES Program

Authorize & oversee
- Majority of states
- Issue of permits

Directly implement
- ID, NM, MA, and NH
- Federal facilities
- Indian country lands

CWA → EPA → NPDES Program
NPDES Permits Required

Discharge Categories

• Municipal wastewater overflows and stormwater management
• Pretreatment
• Stormwater
• Concentrated animal feeding operations (CAFO)
• Biosolids
Wastewater Discharge Programs

Wastewater sources
- Household
- Commercial buildings
- Industry

Pretreatment
- Technology-based effluent limits
- BPT for conventional pollutants (best practical control technology)
- BAT for toxic pollutants (best available technology)
- 115 pollutants “priority pollutants” for water quality criteria

POTW (Public Owned Treatment Works, or Public wastewater treatment plant)

Surface Water
Industry Wastewater Pretreatment: Indirect Discharge

General & Specific Prohibitions
- Pollutants that interfere or pass through POTW
- The Federal sets limits
  - 40 CFR 403.5(a)&(b)

Categorical Pretreatment Standards
- Industry-specific pollutants
- The Federal sets limit
  - 40 CFR 403.6 & Parts 405-71

Local Limits
- More stringent with local needs after the above limits
- POTW sets limits
  - 40 CFR 403.5(c)
Typical Wastewater Treatment Plant (POTW)

Primary treatment (screening and clarification)
- Suspended solids
- Organic matter

Secondary treatment (Biological process)
- Additional suspended solids
- Bio-degradable organics

Tertiary treatment (nitrification/denitrification, activated carbon absorption)
- Other pollutants

Source: EPA March 2015
Technical Development Document for Proposed Effluent Limitations Guidelines and Standards for Oil and Gas Extraction
## Typical Composition of Untreated Domestic Wastewater

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentrations (mg/L)</th>
<th>Weak</th>
<th>Moderate</th>
<th>Strong</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDS</td>
<td></td>
<td>270</td>
<td>500</td>
<td>860</td>
</tr>
<tr>
<td>COD</td>
<td></td>
<td>250</td>
<td>430</td>
<td>800</td>
</tr>
<tr>
<td>TSS</td>
<td></td>
<td>120</td>
<td>210</td>
<td>400</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td></td>
<td>110</td>
<td>190</td>
<td>350</td>
</tr>
<tr>
<td>TOC</td>
<td></td>
<td>80</td>
<td>140</td>
<td>260</td>
</tr>
<tr>
<td>Oil and grease</td>
<td></td>
<td>50</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Chlorides</td>
<td></td>
<td>30</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>Nitrogen total</td>
<td></td>
<td>20</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>Sulfate</td>
<td></td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Phosphorus, total</td>
<td></td>
<td>4</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>Nitrates</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nitrites</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Source:** EPA March 2015 Technical Development Document for Proposed Effluent Limitations Guidelines and Standards for Oil and Gas Extraction

**Legend:**
- **TDS**: total dissolved solids
- **COD**: chemical oxygen demand
- **TSS**: total suspended solids
- **BOD**: biochemical oxygen demand
- **TOC**: total organic carbon
Metals Regulated in Wastewater Effluent (40 CFR 401.15)

12 metals are on the list
Analytical Challenges for Wastewater

- High matrix: multiple elements/contaminants
- Wide dynamic range: high concentration (1000 ppm down to a few ppb)
- Variation of sample types may need different method development
- Multiple interferences need to be overcome
- High throughput of sample analysis maybe negatively impacted from contract labs
- Approved methods with high sensitivity and instruments that overcome high matrix challenges are necessary
Solutions to Improve Matrix Tolerance

**Technical Note 43202**

Analysis of High Matrix Samples using Argon Gas Dilution with the Thermo Scientific ICAP Q ICP-MS

David Kuchta, Julien D. Wills, Shane McInerney, Duquesne, Thermo Fisher Scientific, Bremen, Germany

**Key Words**

Argon Gas Dilution, AGD, High Matrix Samples, Isolator

**Goal**

To critically assess the use of Argon Gas Dilution (AGD) on the Thermo Scientific ICAP Q ICP-MS for the direct analysis of high matrix samples such as Isolator.

**Introduction**

High matrix samples remain a challenge in ICP-based applications. For example, high levels of dissolved solids can cause ionization suppression that reduces sensitivity during the analysis of real samples by both ICP-OES and ICP-MS. In ICAP-Q, the situation is further complicated as high matrix levels may lead to blockage of the narrow aperture cone used to interface the plasma to the mass spectrometer. While continual advances in interface design have improved suggestions, manual sample dilution and a suitable solvent is usually used to reduce sample matrix levels to ≤ 40 mL saline-diluted solids (SDS) before ICP-MS analysis. Depending on both the application and required sample throughput level, this may not be feasible as it increases both the risk of contamination and the cost per analysis (due to the additional time and consumables). Argon Gas Dilution (AGD) is a useful technique to address these fundamental limitations. In AGD ICP-MS analysis, the argon (Ar) gas flow through the nebulizer is reduced while the total Ar gas flow to the plasma is maintained by the addition of a make-up Ar gas flow to the aerosol forming the sprayer chamber. The sample aerosol is therefore diluted with Ar gas inside the ICP-MS sample introduction system. Since the absolute amount of sample entering the plasma is limited, the dissolution of heavy matrix samples in the ICP is improved, reducing matrix deposition on the ICP-Q interface. Overall, plasma robustness improves in AGD mode as demonstrated by a reduction in matrix-related interferences.

Additionally, dilution with clean Ar gas minimizes contamination by reducing sample handling without increasing analysis times or requiring extra (potentially costly) consumables.

The use of AGD is not, however, without disadvantages. In contrast to automated, sample-specific dilution, all samples are diluted in AGD mode, reducing absolute instrumental sensitivity. Furthermore, since the proportion of sample to Ar delivered to the ICP is reduced, the plasma needs slightly higher power to maintain the ionization efficiency for elements with higher ionization potentials (IPs). This example leads to reduced sensitivities. Approaches to enhance the inherent characteristics of Ar gas based sample dilution, including optimizing the plasma and the addition of excess carbon, are investigated in this note.

**Introduction**

Similar to most solution-based techniques, elemental quantification by inductively coupled plasma mass spectrometry (ICP-MS) involves numerous dilution steps before the analytical run can commence.

A series of calibration standards have to be supplied at concentration levels designed to span the expected content in the samples. These standards are usually prepared by serial dilution from one or more stock standard solutions. Depending on the required calibration range, several dilutions between 10 to 200-fold are usually required. The majority of samples for elemental analysis by ICP-MS are supplied as solids that have to be first brought into solution, for example, by mineral acid digestion. Depending on the sample and digestion procedure required, the samples would then have to be diluted before analysis—usually between 10 to 100-fold.

During the analytical run, however, samples that do not meet the requirements defined by laboratory standard operating procedures (SOPs) may have to be removed from the autosampler rack for additional dilution and subsequent repeat analysis. For example:

- Online measured concentrations to within the calibrated concentration range.
- Eliminate the effect of variable, sample dependent matrix suppression of the analytical signal.

While these dilution steps can be manually performed by a skilled laboratory technician it is both tedious and time-consuming.

**Technical Note 43208**

Automated, Intelligent Sample Preparation: Integration of the ESI prepFAST Auto-Dilution System with the Thermo Scientific ICAP Q ICP-MS

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Thermo Fisher Scientific, Bremen, Germany

**Key Words**

Auto-Dilution, EPA 200.8, ICP-MS, USP 2332

**Goal**

To demonstrate the increase in and reduce manual tasks through automation of the analytical workflow. Through an integrated combination of intelligent software and hardware, demonstrate how auto-calibration and auto-dilution can simplify routine elemental analysis.

**Figure 1.** The Thermo Scientific ICAP Q ICP-MS with integrated ESI PrepFAST Auto-Dilution System.
Analytical Methods for CWA

Analytical methods

Approved methods

Other methods

General purpose methods

Industry-specific methods

Whole effluent toxicity methods

304(h) or Part 136 methods

Part 136 Table IF and IG, Parts 401-503

Part 136 Table 1A

General purpose methods for metals: EPA 200.7, 200.8, 200.9
Solutions for EPA Methods 200.7, 200.8, and 200.9

• Regulatory review
• Detailed interpretation of the methods for easy understanding
• Summary of the protocols and QCs with results
## Mercury Analytical Methods

<table>
<thead>
<tr>
<th>EPA methods</th>
<th>Technology</th>
<th>Program</th>
<th>Sensitivity</th>
<th>Applications</th>
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</thead>
<tbody>
<tr>
<td>EPA 200.8</td>
<td>ICP-MS</td>
<td>CWA</td>
<td>Sub ppb to ppt</td>
<td>Drinking water, wastewater</td>
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<tr>
<td>EPA 245.1</td>
<td>CVAAS</td>
<td>CWA, SDWA</td>
<td>200 ppt</td>
<td>Wastewater, drinking water</td>
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<td>EPA 245.2</td>
<td>CVAAS (automated)</td>
<td>CWA, SDWA</td>
<td>200 ppt</td>
<td>Wastewater, drinking water</td>
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<td>CVAAS</td>
<td>CWA, SDWA</td>
<td>5 ppt</td>
<td>Wastewater</td>
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<tr>
<td>EPA 1630</td>
<td>CVAAS</td>
<td>Not approved</td>
<td>0.02 ppt</td>
<td>Water</td>
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<tr>
<td>EPA 1631E</td>
<td>CVAFS</td>
<td>CWA</td>
<td>0.5 ppt</td>
<td>Wastewater</td>
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<td>EPA 7470A</td>
<td>CVAAS (manual)</td>
<td>RCRA</td>
<td>200 ppt</td>
<td>Solid waste, soils and sludge</td>
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<tr>
<td>EPA 7471B</td>
<td>CVAAS (manual)</td>
<td>RCRA</td>
<td>200 ppt</td>
<td>Solid waste, soils and sludge</td>
</tr>
</tbody>
</table>
EU Industrial Emission Regulations

- UWTD sets minimum treatment standards that urban wastewater treatment plants and industrial users have to meet
- IPPC provides a framework to regulate the industrial sectors with the most polluting activities
- Controls of concentrations in surface water are needed for the priority substances (PS) and priority hazardous substances (PHS) under WFD
Urban Wastewater Treatment Directive

Legend:
Pre-TR = pre-treatment
Agro-food = food-processing industry
UWWTP = urban waste water treatment plant
Agro-food >4000 p.e. = food-processing industry
Art.3, 4, 5, 7, 11, 12, 13, 14 = articles of the Directive 91/271/EEC

Source: UWWD overview

Directive 91/271/EEC
Directive 98/15/EC
Industrial Pollution Prevention and Control

• Establishes a procedure for authorizing both industrial and agricultural activities
• Sets minimum requirements for pollutants released in the permits
• Directive 96/61/EC, then Directive 2008/1/EC
• Based on the following principles
  • An integration approach
  • Best available techniques (emission limit values for permits)
  • Flexibility
  • Public participation
## Metal Measurement in EU Water Framework Directive

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample Preparation</th>
<th>Chromatography</th>
<th>Analyzer</th>
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</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>Stabilization with acid</td>
<td>IC (for speciation)</td>
<td>ICP-OES and ICP-MS</td>
</tr>
<tr>
<td>Lead</td>
<td>Stabilization with acid</td>
<td>-</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Stabilization with acid</td>
<td>-</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>Mercury</td>
<td>Stabilization with acid</td>
<td>IC (for speciation)</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>Nickel</td>
<td>Stabilization with acid</td>
<td>-</td>
<td>ICP-MS GFAA ICP-OES</td>
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</tbody>
</table>
Dealing with High Matrix Environmental Samples: Part 2: Improve Your ICP Instrumentation Uptime—Essential Hints and Tips

October 20, 2015        8 AM PDT        11 AM EDT        16:00 BST

Marcus Manecki
Application Specialist
ICP-MS

Elena Chernetsova, Ph.D.
Application Specialist
ICP-OES

- Different techniques to achieve superior sensitivity/low detection limits and wide dynamic range for complex environmental samples
- Low maintenance and easy clean-up reduces workload and sustains high precision
- How automation can help to save time and money

- Basic laboratory needs with high throughput capability
- Advanced analysis with sample autodilution functions in a high throughput format
- Fast and advanced sample introduction with high throughput analysis
Other Resources on Wastewater Analysis

- Ion chromatography municipal water analysis application summary (AI 70863)
  (http://info1.thermoscientific.com/content/CMD_KL_Resources?kl=WAT_&ce=E.14CMD.DX105.03690.01&iq=IQLAAAGADHFAMJMZZZ#&rid=9701)
  - Application notes for drinking water and wastewater
  - Ion chromatography technology review

- Wastewater analysis page
  - Different solutions to wastewater analysis using different technologies
  - Application notes collection on wastewater analysis

- European water framework directive brochure (BR71154)
  - Recommended analysis technologies for contaminants
  - Sample preparation
  - Technology reviews
Analysis of trade waste effluent by ICP-MS

Brian Walker - Analytical Team Leader

2015
Presentation content

• A brief overview of Sembcorp

• Context in which the ICP is used

• Common issues with high matrix samples

• Focus on Mercury in waste effluent water and the specific problems we have encountered

• How these problems were overcome

• Summary
Sembcorp – a brief overview

• Sembcorp owns and operates one facility in the UK

• Sembcorp Utilities is based on Teesside

• This is a part of the Sembcorp group whose parent company is based in Singapore and is a leading energy, water and marine engineering group.

• Sembcorp has other business interests in Singapore, China, India, Middle East, Brazil, Chile, South Africa and Vietnam.
Sembcorp on Teesside

• The facility on Teesside is based at the Wilton International site.

• This site was originally a single integrated facility developed by ICI in the 1950’s and 60’s.

• Since late 1990’s after the break up of ICI the site infrastructure was owned by Enron and since 2003 it has been owned by Sembcorp.

• Sembcorp built and operates the first large scale biomass boiler in the UK. We are now developing a £250 million (joint venture with SITA) waste to energy plant which is scheduled to be on line during 2016.

• Sembcorp is a utilities and services provider for the site residents which include SABIC, Huntsman, Lotte Chemicals, Ensus and others.
Sembcorp Analytical Services

- The laboratory is ISO17025 accredited for a range of testing including trade waste effluents, biomass for Sembcorp power station and asbestos.
- Other testing is carried out which includes Occupational Hygiene and Sounds monitoring which is covered within the ISO9001 accreditation.
- The effluents monitoring is carried out daily as the site drains discharge directly to the River Tees with no pre-treatment.
- A range of compliance testing on this effluent is carried out using analytical techniques such as Headspace GC-MS, TOC, ICP-MS, IC, BOD and a range of wet chemistries.
- In addition to this compliance analysis the site drains are independently sampled and tested by the Environment Agency on a weekly basis to assess the discharge from site.
Tees estuary showing industrial complexes – Wilton International site is outlined
Operating an ICP-MS

The ICP-MS is a sophisticated technique and requires a greater degree of user input than many traditional Analytical techniques. With this in mind it is important to establish robust methods and procedures when carrying out routine analysis.

The methods for ICP established at Sembcorp have been developed to ensure that samples can be prepared and analysed as soon as possible after arriving in the lab.

The earlier slides discussed the range of techniques used to monitor the site effluent and to ensure effective effluent controls are maintained, results for all samples are required on the same day as the sample was received. The speed of analysis and timely reporting of results allows control measures to be put in place in the event of any issues.
ICP Instruments

The current accreditation for metals in trade waste effluent is for the use of ICP-MS.

The lab has recently replaced in 2015 a Thermo Scientific™ X series 2 with the Thermo Scientific™ iCap™ Q ICP-MS system.

In addition to this instrument the lab also has an iCap duo 6300 OES – This instrument is currently being validated for trade waste effluent analysis with a view to gaining ISO17025 accreditation.

**Analytes of interest are V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Hg and Pb.**

The detection limit for Hg using ICP-OES is >20ug/L and this instrument is not used to assess this analyte. All other detection limits are adequate for the effluent applications we have.
Sample Preparation – Issues to consider

◆ What is the Total Dissolved Solid (TDS) content of the sample?

◆ Does the sample require additional digestion, which acid should you use?

◆ Do you need to filter the sample after digestion?

◆ Does the sample preparation stage add interferences to your solution?
Sample preparation

◆ High TDS?
This can be overcome by sample dilution with water but this does reduce Limit of Detection (LOD). Argon aerosol dilution can be utilised but again this reduces LOD. Compromise is required to overcome this problem.

◆ Which acid to use?
Nitric acid is preferred but Hydrochloric is also commonly used. HCl can lead to Cl interferences with transition elements. Other acids are used but these also have other problems to overcome with their use.

◆ Sample Filtration?
Can increase the risk of blockages in the tubing and nebuliser if the samples are not filtered. Carry out checks on sample blanks and spiked blanks to verify the filter does contaminate your sample.
Common problems with High matrix samples

◆ High TDS which can cause solid deposition on the cones leading to signal suppression (diagram below). This can be observed by using Internal Standard (IS) solution mixed with the sample prior to the nebuliser. An 80-120% recovery is required for all IS components.

◆ Salts blocking the nebuliser – sample dilution with water reduces this possibility.
Instrument set up at Sembcorp

◆ Three Internal Standards are used across the mass range Sc, Rh and Ir. The quantities of each are based on anticipated levels of impurities in the typical sample. Results are quantified by interpolation of the three Internal Standard elements.

◆ Analysis is performed in Kinetic Energy Discrimination (KED) mode using Helium to minimise polyatomic interferences. Oxide ratios are controlled and accounted for during the instrument Performance checks prior to analysis.

◆ Peristaltic pump rate of 20rpm to control the sample introduction to the spray chamber was found to be the optimum

◆ Plasma conditions are standard – these will be dependent on your sample matrix.
Mass selection of elements

This is dictated by a number of requirements such as

- Interferences from **polyatomic** (combination of sample and matrix ions with Argon and other matrix components) and **isobaric** (equal mass isotopes of different elements present in the sample) sources as shown in the table below for Nickel which may be present in the sample matrix.

- Relative abundance of the chosen isotope and detection limit requirements

<table>
<thead>
<tr>
<th>Isotope</th>
<th>% Abundance</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 Ni</td>
<td>67.8</td>
<td>23Na35Cl+, 40Ar18O+, 40Ca18O+, 40Ca17O1H+, 42Ca16O+</td>
</tr>
<tr>
<td>60 Ni</td>
<td>26.2</td>
<td>44Ca16O+, 23Na37Cl+, 43Ca16O1H+</td>
</tr>
<tr>
<td>61 Ni</td>
<td>1.3</td>
<td>44Ca16O1H+, 45Sc16O+</td>
</tr>
<tr>
<td>62 Ni</td>
<td>3.7</td>
<td>46Ti16O+, 23Na39K+, 46Ca16O+</td>
</tr>
<tr>
<td>64 Ni</td>
<td>1.1</td>
<td>32S16O2+, 32S2+</td>
</tr>
</tbody>
</table>
ICP-MS mercury determination – background information (data based on X series 2 icp-ms)

• The method for determining Mercury has been validated and an LOD of 0.1 ppb was determined. Historically Mercury has been reported to be <0.1 ppb. The instrument used for this analysis was a Thermo X series 2.

• The method is ran in KED mode using He to minimise any interferences. Internal standards of Scandium, Iridium and Rhodium are used to provide cover across the mass ranges for the other components we monitor. Mass 202 is used to determine Hg. This is the most abundant isotope and also has no other elemental interferences.

• Standards and samples are “doped” with Gold (~40 ppb) to maintain any Mercury in solution. Gold is a strong oxidizing agent which maintains the mercuric ion in solution. (US EPA – Stabilisation of mercury in water samples)

• As part of the ISO17025 accreditation we also take part in the Aquacheck PT scheme (LGC) for trade waste effluents with Mercury being one of the nominated analytes of interest.
Aquacheck PT scheme - observations

• Typically there are approximately 40-50 laboratories submitting data for Mercury determination in this scheme. The test range is typically between 5 and 24 µg/L.

• A range of techniques are used by the different labs including ICP-MS, ICP-OES, Hydride generation/Cold vapour technique

• Our PT data has been consistently good with Z score <2 for 17 consecutive rounds although typically we have reported with a slight negative bias during this time period.

• Typically in each round approximately 20-25% of participants obtain a z score >2.

It’s fair to say that Mercury can be a difficult element to quantify accurately.
Aquacheck PT scheme – last 17 z scores

\[ z\text{ score} = \frac{x-X}{SDPA} \]

- \( x \) – participant result
- \( X \) – the assigned value
- \( SDPA \) – standard deviation for proficiency assessment
Mercury problems in “day to day” samples - observations

• We had observed that recoveries of the Mercury standard at the end of a typical daily test sequence was prone to dropping below 80%. Other monitored metals did not demonstrate this problem.

• The sample prior to this system check standard on each occasion was a duplicate of the first sample in the sequence. The mercury value in this repeat sample was often not a “good” duplicate, other metals were all ok.

• The recovery of the Mercury was not consistent on a “day to day” basis.

• Needed to have a method with a Limit of Detection of <0.5 ppb
Investigations around this issue concluded that the site effluent matrix was not consistent on a “day to day” basis, with a varying salt concentration being present. (mainly Sodium and Calcium salts)

Primarily this variability was due to a reduced number of businesses discharging effluent and some businesses were manufacturing on a campaign basis causing discharges to vary over time.

The method was originally developed when there was a greater volume of effluent being discharged on a more continuous basis. These effluent streams did not have the same matrix effect we were now observing.

The method no longer met requirement – an improved method was required. Ideally an LOD of <0.5ppb was required.
Method evaluation

- Using the lowest calibration standard (1μg/L) to verify the method was capable of achieving the 0.1ppb LOD a 3σ LOD of 0.09μg/L was achieved.

- A series of 10 samples from the same effluent source (diluted 1:1 with 18MΩ water) were run and an average value of -0.24ppb was recorded. This observed negative value increased during the run sequence.

- The same sample and dilution was carried out with a 1ppb spike of Mercury introduced into the sample.
Method evaluation

• From the 10 samples run in the sequence – the first result was 0.79ug/L and the last result in sequence was 0.55ug/L.

• The observed %RSD was 12.5% and an average Hg recovery of 63.9% was obtained from this sample sequence.

• Based on this data the LOD would be 0.24ppb (3 times SD)

• In both sequence runs the recoveries of the three internal standards was not consistent from sample to sample also indicating some effects from the matrix.
Mercury recovery on 10 replicate samples with 1:1 dilution

Hg 1 ppb spike

© Sembcorp Industries 2013
Method evaluation

• The same technique of spiking was employed but a greater level of sample dilution was introduced (1:4) to minimise matrix effect.

• This gave more consistency with the internal standards but the recovery of Hg varied from the first result in the sequence of 0.87ppb to the last 0.31ppb.

• The average recovery for Hg in this sequence was 47%.

• This demonstrated that the mercury losses were still occurring despite the dilution effect.
Method evaluation

• An assumption was made that the mercury present in solution was being retained on the sample introduction system as the other species of interest were not being affected.

• The same samples (1:4 dilution) were run with a 1ppb Hg spike to observe any retention effects on the sample introduction system. One sample was excluded as the autosampler did not locate the tube correctly.

• The average recovery of Hg in the sample was 94.6% and a spread of results from 1.19ppb to 0.82ppb was observed. %RSD is 12%. LOD is 0.35 based on 3xSD.

• The recovery of each of the three internal standards was also more consistent with this technique and all were in the range 90 – 110%. Typically they should be in the range of 80-120%
Mercury recovery with 1:4 dilution
Mercury recovery with 1:1 dilution and 1ppb wash solution

• Applying the same principles and utilising a “1ppb mercury wash” between 1ppb spiked samples a 1:1 dilution was performed to maximise the LOD. (The 1ppb wash was prepared from the standard blank solution).

• The levels of Mercury in the rinse solution were monitored to observe any “carry-over” effects between samples. Values between 1.0 and 0.93 were observed for the wash solution Hg.

• The observed recovery of Mercury in the sample matrix was 94.4% with an RSD of 4.4%

• Using 3 x SD the LOD was calculated to be 0.12
Mercury recovery with 1:1 dilution and 1ppb wash solution
Investigation of Hg carry-over effects

- Having confirmed adequate recoveries of Mercury from the sample matrix and “spiked wash” we needed to verify that Mercury was not being carried forward through the system.

- This was assessed using a 2% Nitric acid solution spiked with 1ppm Au and running this solution as a sample in between 1ppb Mercury samples.

- The observed data confirmed that there was no carry-over effect from the Mercury in the system.

- All of the 2% Nitric acid samples gave results between 0.0 and -0.05ppb while the 1ppb Mercury samples gave results ranging from 0.92 to 1.07 ppb.
Investigation of Hg carry-over effects

- 1ppb rinse, Hg ppb
- Wash (2% HNO3, 1ppm Au (aq.))
Routine system maintenance to ensure good performance

- Replace peristaltic tubing regularly

- Check performance in both KED and Standard mode daily to identify potential issues early.

- Carry out regular flushes of the sample tubing with a nitric acid/gold rinse if working with Hg.

- Routine checks on cones and glassware – wash with 18MΩ water.

- Periodic checks of spiked Hg recoveries to monitor matrix effects to ensure ongoing suitability of the method.
Summary

• Mercury presents specific problems that most other elements do not.

• The new method has achieved a LOD of <0.5 ppb

• The “1ppb mercury wash” solution was incorporated into the method successfully. One consequence is a longer run time which is tolerable for our lab. This could present problems for labs with high throughput requirements.

• Do we know why the Mercury and not the other analytes is affected in the system?

Possibilities

• My own theory is that in our samples Mercury is “retained more strongly” on the sample introduction system with high matrix samples. By adding regular “spikes” of Mercury we are ensuring these “retention sites” are occupied and any Mercury present in the sample is able to pass into the plasma.
Comparison of X series and iCap Q System

- We have observed an increased sensitivity of 5 to 10 times for most elements when operating in KED mode.

- The effluent analysis methods are currently being validated but we are anticipating an ability to determine Hg at 0.02ug/L in the High Matrix samples we handle.

- User access for routine maintenance is much improved in the iCap-Q due to the “pull down” door housing the cones and ion lens.

- For labs using both the Thermo MS and OES systems there are a number of benefits to the current version of software as the visual interface and user options are very similar in both systems making training of users simpler.
Thank you for joining me in this presentation. I hope it has been useful. Preparing this presentation has helped me to understand how much more there is to learn about ICP.

One thought to bear in mind is that “the only stupid question is the one you do not ask”.

I am grateful to Thermo Fisher Scientific for inviting me to share this presentation with you. I would also like to express my thanks to the various people at Thermo Fisher Scientific in the UK for their help and patience over the years.

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Other Resources on Wastewater Analysis

• Ion chromatography municipal water analysis application summary (AI 70863)
  (http://info1.thermoscientific.com/content/CMD_KL_Resources?kl=WAT &ce=E.14CMD.DX 105.03690.01&iq=IQLAAAGADHFAMJMZZZ#&rid=9701)
  • Application notes for drinking water and wastewater
  • Ion chromatography technology review

• Wastewater analysis page
  • Different solutions to wastewater analysis using different technologies
  • Application notes collection on wastewater analysis

• European water framework directive brochure (BR71154)
  • Recommended analysis technologies for contaminants
  • Sample preparation
  • Technology reviews