Improving Trace Elemental Analysis

- Improve Detection Limits
- Sample Pretreatment, Separation
  - Analyte Preconcentration
  - Matrix Removal
  - Interference Removal
  - Wavelength
  - Isotope
    - Isobars
    - Molecular ions
    - Mass discrimination effects

\[
\begin{align*}
\text{Log(detection limit)} & \quad \text{Log(abundance)} \\
-2 & \quad -1 \quad 0 \quad 1 \quad 2 \\
2 & \quad 3 \quad 4 \quad 5
\end{align*}
\]

Crustal Abundance

\[\text{M. Thompson, Analyst, 110, 443-449 (1985).}\]

\[
\begin{align*}
\text{Log(detection limit)} & \quad \text{Log(abundance)} \\
-2 & \quad -1 \quad 0 \quad 1 \quad 2 \\
2 & \quad 3 \quad 4 \quad 5
\end{align*}
\]

Relationship between ICP-AES detection limit (µg/g) and crustal abundance (µg/g) for a number of elements after dissolution with dilution factor of 1000

\[\text{M. Thompson, Analyst, 110, 443-449 (1985).}\]

\[
\begin{align*}
\text{Log(detection limit)} & \quad \text{Log(abundance)} \\
-2 & \quad -1 \quad 0 \quad 1 \quad 2 \\
2 & \quad 3 \quad 4 \quad 5
\end{align*}
\]

Relationship between ICP-AES detectability (µg g⁻¹) and quantifiability, and mean abundance (µg g⁻¹) of various elements in land plants.

\[\text{M. Thompson, Analyst, 110, 443-449 (1985).}\]

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\begin{align*}
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\end{align*}
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Relationship between ICP-AES detectability (µg g⁻¹) and quantifiability, and mean abundance (µg l⁻¹) of various elements in river waters.

\[\text{M. Thompson, Analyst, 110, 443-449 (1985).}\]

\[
\begin{align*}
\text{Log(detection limit)} & \quad \text{Log(abundance)} \\
-2 & \quad -1 \quad 0 \quad 1 \quad 2 \\
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Relationship between ICP-AES detectability (µg g⁻¹) and quantifiability, and mean abundance (µg l⁻¹) of various elements in river waters.

\[\text{M. Thompson, Analyst, 110, 443-449 (1985).}\]
Sample preparation is necessary to isolate the desired components from complex matrices, because most analytical instruments cannot handle the matrix directly. Recent trends in sample preparation include:
- Miniaturation
- Automation
- High-throughput performance
- On-line coupling with analytical instruments, and
- Reduction in solvent volume and time

Reviews recent advances in sample preparation techniques for forensic, clinical and pharmaceutical analysis, with special focus on in-tube solid-phase microextraction and related new techniques.
Sample Preparation

- Concentration adjustment
  - Analyte preconcentration
- Sample clean-up
  - Matrix removal
- Criteria
  - Minimal sample loss, good analyte recovery
  - Efficient removal of coexisting compounds
  - Convenient and rapid procedure
  - Low cost
  - Subsequent analysis step unaffected


Liquid-Liquid Extraction (LLE)

- Traditional liquid-liquid extraction
  - Most widely used sample pretreatment method for liquid samples
  - Good reproducibility and large sample capacity
- Drawbacks of liquid-liquid extraction
  - Solvent selection
  - Requires large amounts of high purity solvents
  - Expensive and toxic
  - Produces hazardous laboratory waste
  - Time- and labor-intensive procedure
  - Tendency to form emulsions
  - Poor potential for automation
  - Multi-step methodology
  - Analyte loss, recovery
  - Sample preparation the major source of analysis errors

Developments in Single-Drop Microextraction

"As someone who did a lot of development work measuring metals in seawater, and shook way too many separatory funnels over the years, I think the on or off line column systems are a lot nicer than organic extraction".

– Rob Franks, Scripps, June 25, 2004

Recent Extraction Techniques for Solid Matrices – Supercritical Fluid Extraction, Pressurized Fluid Extraction and Microwave-Assisted Extraction: Their Potential and Pitfalls
Valérie Camel, Analyst, 126, 1182-1193 (2001)

- Optimization strategies
- Supercritical fluid extraction
- Pressurized fluid extraction
- Microwave-assisted extraction
- Comparative performance
- Matrix effects
- Selectivity
- Automation
- Operating procedure complexity
- Selecting the right technique for the right application
- Future trends

Valérie Camel, Analyst, 126, 1182-1193 (2001)
Pressurized Fluid Extraction (PFE) as an Alternative General Method

Table 1: Parameters influencing the recent techniques and optimization strategy

<table>
<thead>
<tr>
<th>Technique</th>
<th>Parameter</th>
<th>Main effect</th>
<th>Optimization strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFE</td>
<td>Nature of the solute</td>
<td>Aqueous</td>
<td>Sublimation</td>
</tr>
<tr>
<td></td>
<td>Valency of the solute</td>
<td>Ionic</td>
<td>Sublimation</td>
</tr>
<tr>
<td>Extraction parameters</td>
<td>Pressure</td>
<td>Sublimation</td>
<td>Increase pressure</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>Sublimation</td>
<td>Decrease efficiency</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>Excess</td>
<td>Increase extraction time</td>
</tr>
<tr>
<td>Nature of the matrix</td>
<td>Large particles</td>
<td>Low extraction rate, low recoveries</td>
<td>Grind the matrix</td>
</tr>
<tr>
<td></td>
<td>Small particles</td>
<td>More extraction, low recoveries</td>
<td>Decrease extraction rate</td>
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<tr>
<td></td>
<td>Small particles</td>
<td>More extraction, low recoveries</td>
<td>Decrease extraction rate</td>
</tr>
<tr>
<td>MAE</td>
<td>Nature of the solute</td>
<td>Aqueous</td>
<td>Sublimation</td>
</tr>
<tr>
<td>Extraction parameters</td>
<td>Temperature</td>
<td>Sublimation</td>
<td>Increase extraction rate</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>Excess</td>
<td>Increase extraction time</td>
</tr>
<tr>
<td>Nature of the matrix</td>
<td>Large particles</td>
<td>Low extraction rate, low recoveries</td>
<td>Grind the matrix</td>
</tr>
<tr>
<td></td>
<td>Small particles</td>
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</tr>
</tbody>
</table>

Valérie Camel, Analyst, 126, 1182-1193 (2001)

Parameters Influencing Technique and Optimization Strategy

- Nature of solute
- Extraction parameters
- Nature of matrix

Future Trends

Valérie Camel, Analyst, 126, 1182-1193 (2001)

- Supercritical fluid extraction – High potential selectivity at mild conditions
- Pressurized fluid extraction
  - One commercial system (ASE)
  - Growing interest
  - Less selectivity required and several matrices
  - Convenient to use, automation
  - Expect increased development
- Microwave-assisted extraction
  - Two PMAE systems available
  - Less selectivity required and several matrices
  - Multiple simultaneous extractions at moderate conditions
  - Expect increased development

General Optimization Strategy for Extraction Conditions

Comparison of Extraction Procedures for the Determination of Arsenic and Other Elements in Lobster Tissue by ICP-MS

Judith A. Brisbin and Joseph A. Caruso

- A variety of extraction procedures evaluated
- Soxhlet
- Room temperature mixing
- Sonication
- Microwave assisted (MAE)
- Supercritical carbon dioxide
- Subcritical water extraction

- In general, microwave assisted extraction gave comparable or improved recoveries for all of the analytes monitored and usually required less solvent
- MAE proved to be the mildest, fastest, least complicated, and most reproducible extraction technique evaluated
- MAE at 75°C for 2 min exposure time gave quantitative recovery of arsenic from TORT-2
- Extraction efficiencies might have some dependence upon the extraction technique, extraction conditions, analyte, solvent, and sample matrix.
Supercritical Fluid Extraction: A Critical Review of its Analytical Usefulness

Supercritical Fluid Extraction of Mercury Species
• Supercritical fluid extraction was used to recover organic and inorganic mercury species
• Variations in pressure, water, methanol, and chelator create methods that allowed separation of inorganic from organic mercury species
• When extracted using a compromised set of extraction conditions, the order of extraction was methyl, phenyl and inorganic mercury
• For the individually optimized conditions, quantitative recoveries were observed
• Level as low as 20 ppb were extracted and then determined using ICP

Main Extraction Techniques for Gas, Liquid, Solid Samples

New Liquid Extraction Approaches
• Solvent microextraction technology
  – Single-drop microextraction (SDME)
    • Simple, inexpensive, fast, efficient, ~ solvent free
  – Liquid-liquid(-liquid) microextraction LPME
• Flow injection extraction (FIE)
  – Low cost, high extraction speed, reduced sample and solvent (~200 µL) consumption
• Solid phase microextraction (SPME)
  – Solvent-less, coated fused silica fiber

Developments in Single-Drop Microextraction
Developments in Single-Drop Microextraction

- The continuous quest for novel sample preparation procedures has led to the development of new methods, whose main advantages are their speed and negligible volume of solvents used.
- The most recent trends include solvent microextraction, a miniaturization of the traditional liquid-liquid extraction method, where the solvent to aqueous ratio is greatly reduced.
- Single-drop microextraction (SDME) is a methodology that evolved from this approach.
- Single-drop microextraction is a simple, inexpensive, fast, effective and virtually solvent-free sample pretreatment technique.
- This article provides a detailed and updated discussion of the developments, modes and applications of single-drop microextraction, followed by a brief description of the theoretical background of the method.
- Finally, the most important parameters as well as some practical considerations for method optimization and development are summarized.


Method Optimization

- Extraction solvent
- Extraction time
- Organic drop volume
- Salt addition
- Sample agitation
- Practical considerations – Syringe type, bubbles, dead volume, positioning, flow pattern


**Single-Drop Microextraction Combined with Low-Temperature Vaporization ICPMS for the Determination of Trace Be, Co, Pd, and Cd in Biological Samples**

<table>
<thead>
<tr>
<th>Element</th>
<th>Method a(pg/mL)</th>
<th>Method b(pg/mL)</th>
<th>Actual Enrichment Factor</th>
<th>RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.12</td>
<td>0.072</td>
<td>160</td>
<td>16</td>
</tr>
<tr>
<td>Co</td>
<td>0.99</td>
<td>0.56</td>
<td>125</td>
<td>14</td>
</tr>
<tr>
<td>Pd</td>
<td>1.5</td>
<td>0.83</td>
<td>40</td>
<td>14</td>
</tr>
<tr>
<td>Cd</td>
<td>0.27</td>
<td>0.16</td>
<td>180</td>
<td>11</td>
</tr>
</tbody>
</table>

*Note: a Cycle-flow, b Continuous-flow extraction method, 0.2 mL/min*


**Determination of Arsenic by Electrothermal AAS Using Headspace Liquid Phase Microextraction After in situ Hydride Generation**


- Arsenic species converted to arsine in 3 mol dm$^{-3}$ HCl sample solution by sodium tetrahydroborate (NaBH$_4$) in a closed headspace vial
- As reacted with AgDDC dissolved in a 4 µl microdrop mixture of 1:3 pyridine:benzyl alcohol suspended in the tip of a microsyringe during a 7 min extraction time at 35°C
- After the equilibrium reached between the arsine in the headspace and microdrop, microdrop transferred to GFAAS
- Enrichment factor 150 X (4 µl from 2 ml sample)

**Developments in Liquid-Phase Microextraction**


- Recent research trends involve miniaturization of the traditional liquid-liquid extraction principle by reducing the acceptor-to-donor phase ratio
- An emerging techniques is liquid-phase microextraction (LPME)
  - A hollow fibre impregnated with an organic solvent used to accommodate or protect microvolumes of acceptor solution
- This novel methodology proved to be
  - A simple, low-cost and virtually solvent-free sample-preparation technique
  - Provided a high degree of selectivity and enrichment by additionally eliminating the possibility of carry-over between runs
- Different LPME modes and hollow-fiber configurations and up-to-date summary of its applications described
- The most important parameters and practical considerations for method optimization are also discussed
- LPME compared with solid-phase microextraction (SPME) and single-drop microextraction (SDME)

**Solvent Microextraction**

- Solvent microextraction technology
  - Liquid-liquid-liquid microextraction (LPME)
    - Immiscible liquid films (2-, 3- phase)
    - Fast, effective, low-cost, ~ solvent free
  - Membrane-based extraction (MBE)
    - Porous and non-porous membranes
  - Single-drop microextraction (SDME)
    - Simple, inexpensive, fast, efficient, ~ solvent free
  - Solid phase microextraction (SPME)
    - Solvent-less, coated fused silica fiber
  - Flow injection extraction (FIE)
Membrane Extraction Micro-LLE

- Porous membrane techniques
  - Solutions on both sides of the membrane in physical contact through the pores of a membrane

- Non-porous membrane techniques
  - Membrane forms a separate phase (polymeric or liquid) between the donor and acceptor solutions

- Supported liquid membrane (SLM) new (1999) technique in non-porous membrane extraction
  - Uses the pores of the polymeric membrane to support an organic solvent
  - A three-phase system with the organic solvent layer sandwiched between the donor and acceptor aqueous solutions
  - Microporous membrane liquid-liquid extraction (MMLLE) one of the phases (usually the acceptor) also an organic solvent, a two-phase system


Membrane Extraction Micro-LLE

- Membrane advantages
  - high selectivity, clean extract formation, a high degree of enrichment
  - trace analysis facilitated by reduced solvent consumption
- Polymeric membrane units either flat or hollow fibers
- Most techniques connect membrane extraction units on-line to analytical instruments


LPME (MBE) Applications

- Biomedical
  - Drugs in biological fluids
  - Coupled to GC, CE, HPLC
- Environmental and food analysis
  - Herbicides, pesticides, PAH in waters, soil slurries, milk


LPME vs. SDME

- SDME
  - Comparable to 2-phase LPME
  - Simple, low-cost, fast extraction
  - Requires careful, elaborate manual operations
  - Rather poor sensitivity and precision, limited extraction time
  - Extra filtration needed with complex matrices
- LPME
  - Organic phase (acceptor) protected by fiber
  - Hollow fiber decelerates organic dissolution into bulk solution
  - Rod-like surface area larger than SDME droplet


LPME vs. SPME

- LPME
  - Extended compound range with 2-, 3- phase modes
  - Inexpensive, disposable hollow fiber
  - Small pore size, microfiltration, clean extracts
  - Variation of length, wall thickness
  - Ionic strength, pH do not influence repeatability, fiber condition
- SPME
  - Simple, solventless, easily automated
  - Applied widely
  - Several types of fibers
  - Limited fiber lifetime, expensive, carryover
  - Sample pretreatment needed for complex matrices
  - Damage in high salt concentrations

New Liquid Extraction Approaches

- Solid phase extraction (SPE)
- Solid phase microextraction (SPME)
- Flow injection extraction (FIE)
  - Low cost, high extraction speed, reduced sample and solvent (~200 µL) consumption
- Solvent microextraction technology
  - Single-drop microextraction (SDME)
  - Liquid-liquid(-liquid) microextraction

Solid Phase Extraction of Trace Elements

- Review
  - Introduction
  - Theory
  - Step-by-step method development guide
  - Applications for selected trace elements

Solid Phase Extraction

- Trace element preconcentration
  - Low natural concentrations
  - High levels of non-analyte constituents
- Liquid-liquid extraction
- Solid phase extraction
  - Reduces
    - Solvent use and exposure
    - Waste disposal
    - Extraction time
  - Conserves analyte species
  - Good preconcentration factors
  - Easily automated
  - On-line coupling to instrumental techniques

Solid-Phase Extraction SPE vs. LLE

- Higher recovery
- More effective concentration
- Less organic solvent used
- No foaming or emulsion problems
- Shorter sample preparation time
- Easier operation
- Easier incorporation in automated process

SPE Operational Steps

Syringe barrel Cartridge Disk

Disposble Sorbent Containers

**Inorganic Cation Binding**

- **Group I “hard” cations**
  - Electrostatic interactions
  - Weak outer-sphere complexes with hard O ligands
  - O < N < S
  - Alkaline and alkaline-earth elements
- **Group II “borderline” cations**
  - Intermediate characteristics
  - Affinity for both hard and soft ligands
  - Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}
- **Group III “soft” cations**
  - Covalent bonding
  - Cd^{2+}, Hg^{2+} strong affinity for intermediate (N) and soft (S) ligands
  - S < N < O

**Solid Sorbent Selection**

- Most critical step
- Ion exchangers now replaced by more selective support with chelating functional groups
- **Sorbents**
  - Hydrophobic supports
    - C_{18}-silica, PS-DVB copolymer
  - Coated solid sorbent
  - Chemical bound solid sorbent
  - Inorganic oxides
Chelating Approaches

- Direct addition of chelating agent
- Chelation retained on sorbents
- Functional groups on sorbents
  - New sorbents
    - Synthesis of sorbents with functional groups
  - Functionalized sorbents
    - Chemical binding of functional groups on existing sorbents
  - Impregnated, coated, loaded sorbents
    - Physical binding of functional groups by impregnating solid matrix with chelating ligand


Advantages of inorganic support
- Good selectivity
- No swelling
- Rapid metal ion sorption
- Good mechanical stability


Chemical Modification of Silica Surface by Immobilization of Functional Groups for Extractive Concentration of Metal Ions
- Mechanically stable synthetic matrices particularly silica gel as a solid support and its surface modification either by impregnation of organic ligands directly or covalent grafting are used for extractive concentration of trace elements
- Functionalized silica synthesis by attachment of various ligands or organic reagents to the silica surface and techniques of characterization of the modified surface developed
- Various modified silica surfaces applied for adsorption of trace elements in complex synthetic mixture and natural water with separation and/or preconcentration


Silica support
- Immobilization on silica results in great variety of silylating agents, allowing pendant functional groups in the inorganic framework
- Attachment is easier on silica surface than on organic polymeric supports, which have a high number of cross-linking bonds, requiring hours to reach equilibrium for surface activation
- Silica gel is the most popular substrate for surface studies, because it is the first commercially available high specific surface area substrate with constant composition enabling easy analysis and interpretation of results
- Silica gel has high mass exchange characteristics and no swelling
- Silica support has great resistance to organic solvents
- Silica has very high thermal resistance

Solid-phase extraction using cartridge and disc devices is a widely used sample-preparation technique for isolation, concentration, clean-up and medium exchange. To meet the varied needs of contemporary applications, an ever-increasing range of sorbent chemistries is available based on inorganic oxides, low-specificity (chemically bonded, porous polymer and carbon) and compound and group-selective (ion exchange, mixed mode, macrocyclic, restricted access, immunoaffinity and molecularly imprinted polymer) materials. Advanced device formats facilitate processing of problem samples combined with a high level of automation. Approaches to computer-aided method development promise to replace tedious trial-and-error procedures with fast simulations based on suitable kinetic and retention models.

New Trends in Solid-Phase Extraction
Colin F. Poole

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- Advanced device formats facilitate processing of problem samples combined with a high level of automation.
- Approaches to computer-aided method development promise to replace tedious trial-and-error procedures with fast simulations based on suitable kinetic and retention models.

SPE Theory
How Compounds Are Retained by the Sorbent

Reversed Phase
(polar liquid phase, nonpolar modified solid phase)
- polar-polar interactions
- hydrogen bonding
- dipole-dipole interactions
- dipole-induced dipole interactions

Normal Phase
(nonpolar liquid phase, nonpolar modified solid phase)
- polar-polar interactions
- hydrogen bonding
- dipole-dipole interactions
- dipole-induced dipole interactions

Ion Exchange
Electrostatic attraction of charged group on compound to charged group on the sorbent’s surface

Adsorption
(Interactions of compounds with unmodified materials)
Hydrophobic and hydrophilic interactions may apply
Depends on which solid phase is used
Active Pipet Tips for SPE

**SPE 255 System**

- Direct Vial Extraction* from VICI Gig Harbor Group

*Vial pending

Direct Vial Extraction (DVE) is a simplified solid phase extraction procedure for environmental sample analysis. Classical methods employed in EPA and Standard Methods for the analysis of drinking water are based on either liquid-liquid extraction or liquid-solid extraction methods employing solid phase extraction disks (SPE) disks. DVEV, an autosampler vial containing a sorbent-enhancing coating such as PDMS becomes the extraction medium. Analytes are trapped by sorption into the polymeric material and then eluted by back-extraction with a small amount of solvent. Extraction may be done in the field and archived for further analysis.

The technique eliminates the need for SPE disks, SPE wash-ups, SPE-disk or SPE cartridges. The small amount of solvent required eliminates the need for expensive thermal desorption devices and allows for simpler injection techniques.
Solid Phase Extraction (SPE) is widely used for the purification of small compound libraries synthesized in solution. Compared to the classic liquid-liquid extraction using the separatory funnel or the preparative HPLC purification, it offers several advantages:

- Reduced lab time
- Easy manipulation
- Lesser amount of solvent required, no disposal of large quantities of organic solvents
- Higher concentration factor
- No problem with the miscibility of solvent
- Easy adaptation to very selective extraction
- Avoids problems such as incomplete phase separations, less-than-quantitative recoveries, and emulsion formation as encountered in liquid-liquid extractions

Reaction mixtures from parallel synthesis can easily be purified in a parallel fashion with commercially available disposable cartridges/thimbles/disks and a vacuum manifold. However, a basic knowledge is necessary of how to perform SPE extractions in an efficient way by selecting the right sorbent (from a variety of reversed, normal, or ion exchange phases), conditioning, selective washing, and eluting the compounds of interest.

Determination of Gadolinium in River Water by SPE Preconcentration and ICP-MS

- ICP-MS determination of
  - Gd diethylenetriaminepentaacetate (Gd–DTPA), Gd, and other rare earth elements (REE) in river water
- Ethylhexylphosphates solid phase extraction (SPE)
- Preconcentration of Gd and REE from water samples
  - Acidified surface water samples (pH <3)
  - Ethylhexylphosphates loaded C18 cartridges
  - 40X enrichment factor

Automatic On Line Preconcentration and Determination of Lead in Water by ICP-AES Using a TS-microcolumn

- Simple, sensitive, low-cost and rapid, flow injection system for the on-line preconcentration of lead by sorption on a microcolumn packed with silica gel functionalized with methoxybisalicylate (TS-gel)
- Metal directly retained on the sorbent column and eluted by EDTA
- Five variables optimized
  - Sample flow rate, eluent flow rate, eluent concentration, pH, buffer concentration
  - Interactions between analytical factors and their optimal levels were investigated using two level factorial and Box–Behnken designs.
- Optimum conditions established for the FI-ICP-AES determination of lead
Simultaneous Speciation of Inorganic Selenium and Tellurium by Inductively Coupled Plasma Mass Spectrometry Following Selective Solid-Phase Extraction Separation

- A new method was developed for the simultaneous determination of inorganic tellurium and selenium species in waters by inductively coupled plasma mass spectrometry (ICP-MS) following selective solid-phase extraction (SPE) separation.
- Under acidic conditions, only selenium(IV) and tellurium(IV) formed complexes with ammonium pyrrolidine dithiocarbamate (APDC), and the complexes were completely retained on a non-polar C18 cartridge.
- Te(VI) and Se(VI) passed through the cartridge and remained as free species in the solution, thereafter being determined by ICP-MS.
- Se(IV) and Te(IV) concentrations were obtained as the respective differences between total selenium and Se(VI), and total tellurium and Te(VI) concentrations.

The Solid-Phase Attraction

Aiding Chromatography
Because traditional SPE is somewhat nonspecific, binding classes of compounds rather than unique molecules, it has most often been used as a preliminary sample purification and concentration step for large-scale liquid–liquid chromatography or as a first step before analysis using a variety of spectroscopic techniques. From this perspective, SPE is merely one of several highly useful methods for sample preparation—an extremely critical although somewhat narrow role.

Replacing Chromatography
More and more today, researchers are working to transform SPE into a replacement for standard liquid–liquid chromatography by developing different solid-phase chemistries to expand the repertoire or hone the specificity of the technique. In fact, the sorbents used in typical SPE are often identical to those used for liquid chromatography. They can be used in typical normal phase, reversed phase, ion exchange, or size exclusion (wide-pore) extraction. These different categories of sorbents are typically produced by chemically bonding specific functional groups to silica gel or a variety of polymeric beads or ion-exchange media (a typical particle is 40 µm in diameter with 60 Å pores).

Moving to Membranes
Although traditional SPE evolved in the form of cartridges or particulates in syringes, all of the advantages of membrane filtration can be adapted to SPE by embedding the solid-phase extraction particles into a flat matrix.
- According to 3M, one of many companies producing SPE products, the use of such membranes “results in a denser more uniform extraction medium than can be achieved in traditional solid-phase extraction.”
- Especially useful is the fact that such disk membranes can greatly increase extraction efficiency and reduce the solvent and sample volumes that can be analyzed, in addition to requiring significantly smaller elution volumes, and thus resulting in improved concentration efficiencies of the purified product.

Tailored Materials for Preconcentration or Separation of Metals by Ion-Imprinted Polymers for Solid-Phase Extraction (IIP-SPE)

- Introduction of ion-imprinted polymers (IIPs) in trace and ultratrace analysis provides breakthroughs in preconcentration or separation chemistry.
- The combination of the above two approaches results in IIPs for SPE (IIP-SPE) and has potential in trace and ultratrace analysis.
- With the preparation of tailor-made materials, IIP-SPE offers an approach to the recovery of valuable and rare metals from lean ores, minerals and dilute solutions, and to the removal of toxic uranium and heavy metal pollutants from industrial wastes.
- This article reviews studies and outlines a future scenario in the rapidly developing and exciting area of IIP-SPE.
**Ion-Imprinted Polymer Synthesis**

- Metal Template
- Complexation
- Polymerization
- Leaching


---

**Research Areas in IIP-SPE**

- A - Lanthanides
- B - Actinides
- C - Noble Metals
- D - Transition Elements
- E - Others


---

**Comparison of Retention or Binding Capacities for Selected Metals by Various Imprinted Techniques**

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Retention-binding capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>0.26</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.22</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.17</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.40</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>3.28</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>31.13</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>21.5</td>
</tr>
<tr>
<td>U(VI)</td>
<td>30.10</td>
</tr>
<tr>
<td>Dy(III)</td>
<td>40.15</td>
</tr>
<tr>
<td>Dy(III)(irradiated)</td>
<td>39.17</td>
</tr>
</tbody>
</table>


---

**IIP-SPE**

- Rapidly developing area
- More stable in harsh environments than SPE columns
- Predetermined selectivity
- Simple, convenient preparation
- Molecular imprinted polymer (MIP) trends
- Problems
  - Poor solubility of analyte (template) in imprinting mixture
  - Slow mass transfer rate in binding and release
  - Bleeding of unleached template ions


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**The Solid-Phase Attraction**

- **Coming Extractions**
  - The future of SPE seems secure
  - Already a mainstay of environmental analysis, it has recently been adapted to the stringent requirements of modern biotechnology automation upon being melded with the ubiquitous 96-well plate by a variety of companies
  - Researchers showed that such a well-plate system could make a valuable front-end purification/concentration step for LC-MS-MS used for the determination of protease inhibitors in plasma and cartilage samples.
  - The technique demonstrated significant improvements in time-saving and in the sensitivity of the MS detection.


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Improving Trace Elemental Analysis

- Improve Limits of Detection
- Sample Pretreatment, Separation
  - Analyte Preconcentration
  - Matrix Removal
  - Interference Removal
    - Wavelength
    - Isotope
      - Isobars
      - Molecular ions
      - Mass discrimination effects


On-line Coupling of Ion Chromatography with ICP-AES and ICP-MS
Andreas Seubert

- Ion chromatography (IC) and atomic spectrometry are sometimes competing and sometimes ideally cooperating techniques
- On-line coupling applications of IC and ICP-AES or -MS
  - Ultra trace analysis utilizing ion exchange as a preconcentration technique via speciation applications taking advantage of the unique element specific detection offered by atomic spectroscopy
  - Classical IC applications with atomic spectrometry as a sensitive and selective detector
- Characteristics of this type of hyphenated technique
  - Simple physical coupling
  - Unique sensitivity for most elements, and
  - Superior selectivity obtainable for specific applications

Technique Limitations

Atomic spectrometry
- Distinguishing among different species containing the same element
- Resolving spectral or isobaric interferences with ICP-AES or low-resolution mass filter ICP-MS
- Determining very low concentrations of trace elements in complex samples

Ion chromatography
- Poor detection sensitivity
- Inadequate resolution of interfering compounds
- Limited selectivity
  - Quaternary ammonia exchange functional groups
  - More selective detection needed

On-line coupling of ion chromatography with ICP-AES and ICP-MS

The Solid-Phase Attraction

- Coming Extractions
  SPE has proven its worth in that it can now be routinely automated for cost effectiveness and efficiency for everything from drug applications (from discovery to cocaine abuse monitoring) to environmental applications (from monitoring pesticides to identifying industrial waste).
- Thus it is obvious that whatever the future holds in improvements of analysis, SPE will accompany each new development, providing its time-honored benefits of analyte purification and concentration with ever more precision and technical ease.

On-line Coupling of Ion Chromatography with ICP-AES and ICP-MS


Advantages
- Closed system, reduced airborne contamination
- Metion-free IC equipment
- Reproducible flow rates

On-line preconcentration techniques
- Matrix elimination
- Ion exchange, chelation preconcentration
- Interference elimination
- Speciation analysis
- Isotope dilution MS applications

Example of the simple replacement of conductivity detection by an ICP-MS. The sample was 555 µl of an ozonized tap water. The self-made column P150497 DMEA was operated with 75 mmol/l NH₄NO₃, pH 6 as eluent at a low rate of 1 ml/min. The detection device was an ICP-MS PQ ExCell in the collision cell mode.

Applications of Chromatographic Preconcentration Techniques for On-Line Coupling IC-ICP(AES,MS) Ordered by Matrix Type

<table>
<thead>
<tr>
<th>Sample/matrix</th>
<th>Separation mode</th>
<th>Chromatographic technique</th>
<th>Preconcentration columns</th>
<th>Detection limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>An, Ag, S, P, Br</td>
<td>Column</td>
<td>Cation</td>
<td>U, Be, Na, Mg, K, Ca, Sr, Ba, Ti, Pb, Zn, Cr</td>
<td>0.2-0.200 ng/g</td>
</tr>
<tr>
<td>Methane, methane</td>
<td>Cation</td>
<td>See as application</td>
<td>SCX (AG 400W)</td>
<td>0.1-0.80 ng/g</td>
</tr>
<tr>
<td>Seawater, marine water</td>
<td>Chelation</td>
<td>Cd, Cu, Hg, Pb, Zn, Ni, Cr, Ti, V</td>
<td>Immunoassay</td>
<td>30-300 ng/g</td>
</tr>
<tr>
<td>Alkali and alkaline earth metals, amino,</td>
<td>Chelation</td>
<td>V, Cr, Ni, Cu, Cd, Hg, Bi</td>
<td>Bioaffinity chromatography</td>
<td>9-90 ng/g</td>
</tr>
<tr>
<td>Seawater, marine water</td>
<td>Chelation</td>
<td>Mn, Zn, Cu, Cd, Pb, Hg, Fe, Mn</td>
<td>Immunoassay</td>
<td>0.001-100 ng/l</td>
</tr>
</tbody>
</table>

On-line coupling of ion chromatography with ICP-AES and ICP-MS


Determination of Bromate and Bromoacetic Acids in Water by Ion Chromatography – ICP-MS


On-line coupling of ion chromatography with ICP-AES and ICP-MS


Table 2

<table>
<thead>
<tr>
<th>Type of eluitor</th>
<th>Mass flow dependence</th>
<th>Sensitivity</th>
<th>Desalination needed</th>
<th>Applicable for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional pneumatic</td>
<td>Yes</td>
<td>Low</td>
<td>Yes</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
<tr>
<td>Bubble flow (gas-bubbling)</td>
<td>Yes</td>
<td>High</td>
<td>Yes</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
<tr>
<td>High efficiency injection (HEI)</td>
<td>Yes</td>
<td>High</td>
<td>Yes</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
<tr>
<td>High pressure injection (HPI)</td>
<td>Yes</td>
<td>High</td>
<td>Yes</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
<tr>
<td>DN</td>
<td>Yes</td>
<td>Low</td>
<td>No</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
<tr>
<td>Self-spray chamber</td>
<td>Yes</td>
<td>High</td>
<td>Yes</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
<tr>
<td>Fritted filter chamber</td>
<td>Yes</td>
<td>High</td>
<td>Yes</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Yes</td>
<td>Low</td>
<td>No</td>
<td>Water-based samples, with limitations on organics</td>
</tr>
</tbody>
</table>

Example of the simple replacement of conductivity detection by an ICP-MS. The sample was 555 µl of an ozonized tap water. The self-made column P150497 DMEA was operated with 75 mmol/l NH₄NO₃, pH 6 as eluent at a low rate of 1 ml/min. The detection device was an ICP-MS PQ ExCell in the collision cell mode.
Applications of On-line Coupling IC-ICP-(AES,MS) for Elimination of Atomic Spectrometry or IC Interferences

<table>
<thead>
<tr>
<th>Sample matrix</th>
<th>Separation mode</th>
<th>Eliminated interference IC</th>
<th>Interference IC</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>As species in air</td>
<td>Arise</td>
<td>$^{40}$Ar/$^{37}$Ar or $^{39}$Ar</td>
<td>-</td>
<td>Prototype of this kind of application</td>
</tr>
<tr>
<td>Mo</td>
<td>Arise</td>
<td>$^{95}$Mo on Tr</td>
<td>Other oxides</td>
<td>Ultra trace determination</td>
</tr>
<tr>
<td>REE, REE oxides</td>
<td>Arise</td>
<td>Oxides and hydroxides of lighter REE or heavier even</td>
<td>Peak oxide due to limited selectivity</td>
<td>Hf, Nb, and tantal oxides gradient</td>
</tr>
<tr>
<td>Transition metals in S and O matrices</td>
<td>Arise</td>
<td>S- and O-based oxidations on Y, Eu, Dy, and Sm</td>
<td>Other oxides</td>
<td>Off-line applications with attempts for on-line coupling</td>
</tr>
<tr>
<td>Sr in human urine and serum</td>
<td>Arise</td>
<td>$^{40}$Sr on $^{88}$Sr and $^{86}$Sr</td>
<td>Other oxides</td>
<td>On-line and off-line coupling</td>
</tr>
<tr>
<td>BrO$_3^-$ in water</td>
<td>Arise</td>
<td>$^{79}$Br on $^{81}$Br</td>
<td>C$_2$H$_2$N$_2$O$_2$</td>
<td>High impact on distilling water</td>
</tr>
<tr>
<td>IO$_3^-$ in water</td>
<td>Arise</td>
<td>$^{79}$I on $^{81}$I</td>
<td>Early eluting ions</td>
<td>Species-related</td>
</tr>
<tr>
<td>Fission products</td>
<td>Arise</td>
<td>$^{95}$Tc on $^{99}$Tc</td>
<td>Other oxides</td>
<td>Retention of aqueous isotopic overlap</td>
</tr>
</tbody>
</table>

The Use of a Suppressor Column for Calcium Removal in the Determination of Iron in Water Samples by Collision Cell ICP-MS
Ruben García Fernández, J. Ignacio García Alonso, and Alfredo Sanz-Medel

- The use of H$_2$ as reagent gas eliminates Ar-based interferences in the determination of Fe by collision cell ICP-MS.
- However, natural water samples may contain high levels of calcium, which interfere in iron determinations by forming CaO$^-$ and CaOH$^-$ polyatomics that are not completely eliminated in the cell.
- To eliminate Ca interferences on Fe, a conductivity suppressor column from a conventional ion chromatography system was connected between the pump and the ICP-MS nebulizer.
- The suppressor column removed > 99.99% Ca for Ca concentrations < 1000 ppm.
- To avoid the simultaneous removal of Fe, water samples were previously spiked with EDTA chelating agent to form a negatively charged complex that was not destroyed in the suppressor column.
- Mineral water samples containing < 260 mg l$^{-1}$ of Ca were analyzed and the method allowed the interference-free determination of low ppb levels of Fe.

Applications of On-line Coupling IC-ICP-(AES,MS) as a Tool for the Speciation of Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Separation modes</th>
<th>Separated species</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Arise/air</td>
<td>$^{30}$Ar</td>
<td>Chromatographic separation of fragile complexes</td>
</tr>
<tr>
<td>As</td>
<td>Arise/air</td>
<td>$^{75}$As/As(V), $^{75}$As</td>
<td>Organic As compounds</td>
</tr>
<tr>
<td>Cr</td>
<td>Arise/air/on</td>
<td>$^{52}$Cr</td>
<td>Slow kinetics of Cr$^{VI}$ to problems</td>
</tr>
<tr>
<td>Hg</td>
<td>Ion pair</td>
<td>$^{201}$Hg</td>
<td>Cationic Hg compounds</td>
</tr>
<tr>
<td>Ni</td>
<td>Arise</td>
<td>$^{58}$Ni/54, $^{54}$Ni, $^{56}$Ni</td>
<td>Toxicity due to $^{57}$Ni</td>
</tr>
<tr>
<td>Se</td>
<td>Arise</td>
<td>$^{77}$Se</td>
<td>$^{77}$Se, $^{75}$Se, $^{73}$Se, $^{71}$Se</td>
</tr>
<tr>
<td>Si</td>
<td>Arise</td>
<td>$^{28}$Si, $^{29}$Si, $^{30}$Si, $^{31}$Si</td>
<td>Undiscovered signals</td>
</tr>
<tr>
<td>Sb</td>
<td>Arise</td>
<td>$^{121}$Sb, $^{123}$Sb</td>
<td>Oxidation of $^{125}$Sb</td>
</tr>
<tr>
<td>Sn</td>
<td>Arise</td>
<td>$^{117}$Sn, $^{119}$Sn, $^{121}$Sn</td>
<td>Oxidation of $^{123}$Sn</td>
</tr>
<tr>
<td>Sn</td>
<td>Arise</td>
<td>$^{117}$Sn, $^{119}$Sn, $^{121}$Sn</td>
<td>Oxidation of $^{123}$Sn</td>
</tr>
</tbody>
</table>

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On-line Coupling of IC and ICP-MS

Advantages
- Simple, fast and powerful sample pretreatment technique
- Very low detection limits and quite good reproducibility
- Large dynamic range of ICP-AES and ICP-MS
- ICP operated with a constant secondary matrix

Disadvantages and limitations
- Not all elements and all species are detectable
  - Limited by the chemistry of the chromatography part and by
  - The features of the spectrometer
- Time consuming technique
  - Ranging from 2 to 20 min per sample
- Large data volume must be handled
  - ca. 100 to 1000 data points per measurement
- High surface area of the separation system
  - e.g., memory effects must be considered

IC and ICP-MS Coupling

Disadvantages and limitations
- Quasi-simultaneous detection of quadrupole ICP-MS
  - Influences accuracy
    - Peak height
    - Isotope ratio
  - Significant relative error with similar peak width and scan time
- Isotope ratio precision limited
  - High noise level of sequential ICP-MS
  - Time dependent isotope ratio shift
    - Time dependent elution signal
    - Different measurement times for isotope masses

Focal Point
Hyphenated Techniques for Elemental Speciation in Biological Systems

Endogeneous Trace Element Species in Biological Systems