Arsenic Speciation in Urine by Solvent Extraction / Graphite Furnace Atomic Absorption Spectrometry and Capillary Electrophoresis / Inductively Coupled Plasma Mass Spectrometry

Ross Wenzel

University of Technology, Sydney
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Abstract

A modified version of the solvent extraction method described by Buchet et al (1980) for partially speciating arsenic in human urine specimens was investigated. It was shown to be a valid means of isolating those arsenicals associated with toxicity and was used to screen subjects with elevated total urinary arsenic levels for toxic arsenicals. This method involves the removal of the toxic arsenicals arsenite (As^{III}), arsenate (As^{V}), methanearsonic acid (MAA) and dimethylarsinic acid (DMAA) from urine by a solvent extraction process. After the addition of concentrated hydrochloric acid and potassium iodide, toxic arsenicals are extracted from the urine into cyclohexane and mixed with a matrix modifier solution of nickel nitrate for analysis by graphite furnace atomic absorption spectrometry (GFAAS). Since, in most subjects, elevated urinary total arsenic levels are due to the presence of non-toxic arsenicals following seafood consumption, partial speciation by solvent extraction / GFAAS is used to confirm or to rule out arsenic poisoning in subjects with elevated total urinary arsenic levels.

A capillary electrophoresis (CE) technique was developed, in which CE was interfaced with an inductively coupled plasma mass spectrometer (ICPMS) to permit the isolation and estimation of major arsenic species in urine and other biological specimens. It was possible to separate 5 arsenicals by CE and to detect, by coupled ICPMS, levels of individual arsenicals corresponding to 0.1 ppm (1.3 µmol/L) arsenic in urine. This CE / ICPMS technique was used to evaluate partial speciation by solvent extraction / GFAAS in a range of artificially prepared standard mixtures of arsenicals, and in urine specimens. It was confirmed that the latter technique is a valid means of assessing subjects suspected of arsenic poisoning because of their elevated total urinary arsenic levels.

Using the CE / ICPMS technique, it was also confirmed in one leukaemic patient, that, in humans, the main urinary arsenicals excreted after acute exposure to arsenite (As^{III}) are DMAA and MAA. In other healthy subjects, it was found that, after seafood consumption, the predominant arsenical present in urine was arsenobetaine. On the basis of these studies, a protocol was defined for the stepwise investigation of urine specimens for inorganic and organic arsenic compounds.
Preliminary studies were also carried out on edible seaweeds, which are known to contain arsenosugars and arsenolipids. Partial speciation, of edible seaweed digests, gave incomplete and variable arsenic recoveries. When the same digests were analysed by CE / ICPMS, the only arsenical found was arsenobetaine, suggesting that arsenosugars and arsenolipids may have been broken down to form arsenobetaine during extraction. Although inconclusive, these results demonstrate the usefulness of CE / ICPMS for evaluating arsenic extraction methods in novel sample matrices.
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<tbody>
<tr>
<td>AMU</td>
<td>Atomic mass unit</td>
</tr>
<tr>
<td>AsB</td>
<td>Arsenobetaine</td>
</tr>
<tr>
<td>AsC</td>
<td>Arsenocholine</td>
</tr>
<tr>
<td>As$^{III}$</td>
<td>Arsenite</td>
</tr>
<tr>
<td>As$^{V}$</td>
<td>Arsenate</td>
</tr>
<tr>
<td>BPI</td>
<td>Bias performance index</td>
</tr>
<tr>
<td>CE</td>
<td>Capillary electrophoresis</td>
</tr>
<tr>
<td>CSV</td>
<td>Comma separated variable</td>
</tr>
<tr>
<td>DIN</td>
<td>Direct injection nebuliser</td>
</tr>
<tr>
<td>DMAA</td>
<td>Dimethylarsinic acid (also known as cacodylic acid)</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediamine tetraacetic acid</td>
</tr>
<tr>
<td>EOF</td>
<td>Electroosmotic flow</td>
</tr>
<tr>
<td>GFAAS</td>
<td>Zeeman graphite furnace atomic absorption spectrometry / spectrometer</td>
</tr>
<tr>
<td>HBA</td>
<td>$p$-hydroxybenzoic acid</td>
</tr>
<tr>
<td>HGAAS</td>
<td>Hydride generation atomic absorption spectrometry / spectrometer</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>ICPMS</td>
<td>Inductively coupled plasma mass spectrometry / spectrometer</td>
</tr>
<tr>
<td>ID</td>
<td>Internal diameter</td>
</tr>
<tr>
<td>MAA</td>
<td>Methanearsonic acid</td>
</tr>
<tr>
<td>MCN</td>
<td>Micro concentric glass nebuliser</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-charge ratio</td>
</tr>
<tr>
<td>OD</td>
<td>Outside diameter</td>
</tr>
<tr>
<td>PaLMS</td>
<td>Pacific Laboratory Medicine Services</td>
</tr>
<tr>
<td>PAO</td>
<td>Phenylarsine oxide</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>TMAO</td>
<td>Trimethylarsine oxide</td>
</tr>
<tr>
<td>TTAB</td>
<td>Tetradecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>TTAOH</td>
<td>Tetradecyltrimethylammonium hydroxide</td>
</tr>
<tr>
<td>TX-100</td>
<td>Triton X100</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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