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

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Masters by Thesis – 2001

Acknowledgements

In preparing this thesis I would like to acknowledge the invaluable contribution and support of the following people and organizations: -

My project supervisors: -

Mr. Graham Hams from Pacific Laboratory Medicine Services for suggesting a suitable project topic and providing guidance throughout.

Dr. Ralph Orwell from the University of Technology, Sydney for thoroughly reading through various drafts of this thesis and identifying ways in which improvements could be made.

Pacific Laboratory Medicine Services for funding this project.

Mr. Steve Toovey from the Biomedical Engineering Department at Royal North Shore Hospital for invaluable technical assistance with the electrical systems used.

Dr. Stephen Anderson from Varian Australia for generous assistance with parts and operational advice.

Pacific Laboratory Medicine Services and Royal North Shore Hospital grants committee for providing funding so that part of this project could be presented at the 17th Australian and New Zealand Society of Mass Spectrometry conference.

Division of Analytical Laboratories, Lidcombe for donating arsenobetaine.

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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List of Abbreviations

AMU	Atomic mass unit
AsB	Arsenobetaine
AsC	Arsenocholine
As^{III}	Arsenite
As^{V}	Arsenate
BPI	Bias performance index
CE	Capillary electrophoresis
CSV	Comma separated variable
DIN	Direct injection nebuliser
DMAA	Dimethylarsinic acid (also known as cacodylic acid)
EDTA	Ethylenediamine tetraacetic acid
EOF	Electroosmotic flow
GFAAS	Zeeman graphite furnace atomic absorption spectrometry / spectrometer
HBA	*p*-hydroxybenzoic acid
HGAAS	Hydride generation atomic absorption spectrometry / spectrometer
HPLC	High performance liquid chromatography
IC	Ion chromatography
ICP	Inductively coupled plasma
ICPMS	Inductively coupled plasma mass spectrometry / spectrometer
ID	Internal diameter
MAA	Methanearsonic acid
MCN	Micro concentric glass nebuliser
m/z	Mass-to-charge ratio
OD	Outside diameter
PaLMS	Pacific Laboratory Medicine Services
PAO	Phenylarsine oxide
PTFE	Polytetrafluoroethylene
RF	Radio frequency
TMAO	Trimethylarsine oxide
TTAB	Tetradecyltrimethylammonium bromide
TTAOH	Tetradecyltrimethylammonium hydroxide
TX-100	Triton X100
UV	Ultraviolet

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