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Occupational and Environmental Exposures of Skin to Chemicals - 2005

Abstract for Poster 20

Urinary biomarkers of 1-bromopropane exposure: evaluation of LC/MS analytical test procedures for quantification

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An LC/MS procedure was evaluated for the quantification of N-acetyl-S-(n-propyl)-L-cysteine (propylmercapturic acid, PMA) in urine. PMA is a metabolite and biomarker for exposure to 1-bromopropane (1-BP; n-propylbromide, CAS Registry no. 106-94-5), an industrial solvent that is being used as a replacement for potential ozone depleting chlorofluorocarbons. 1-BP is a health concern for exposed workers because of reported chronic toxicity. Central neurological and peripheral neuropathy disorders have been reported in workers exposed to 1-BP; reproductive and hematopoietic disorders have been reported in rats. 1-BP is readily absorbed through the skin and of concern for human dermal exposure. Potential biomarkers for the evaluation of 1-BP exposure have been tried with varying degrees of success including urinary bromine, GC/EC analysis of 1-BP, and GC/MS analysis of 3-bromopropionic acid. The major metabolites of 1-BP, however, have been shown to include several mercapturic acids, the products of several metabolic pathways. To evaluate the utility of these as biomarkers, solid phase extraction conditions were developed for sample preparation of urine for the analysis of PMA as well as PMA-S-oxide, N-acetyl-S-(3-hydroxypropyl)-L-cysteine and N-acetyl-S-(2-carboxyethyl)-L-cysteine. LC conditions for chromatographic separation were coupled with electrospray "soft ionization" and mass spectrometry. Positive ion ESI LC/MS/MS product scanning was performed for structural analysis. Initially, a Finnegan MAT LCQ ion trap tandem MS/MS was used to evaluate mercapturic acid formation, and the major 1-BP urinary product, PMA, appeared to be the most useful biomarker. Subsequently, PMA alone was routinely analyzed using an Agilent 1100 LC/MSD SL mass spectrometer system using selected ion monitoring (SIM) in the negative ion ESI LC/MS mode for maximum sensitivity. d_7 -PMA was used as internal standard and samples were extracted using Varian BondElute C18 solid phase extraction (SPE) columns. Sample extracts were injected onto a 150-mm X 2.0-mm (id) Aqua C-18 Phenomenex column and eluted using a water:methanol (0.1% acetic acid) gradient. Optimal instrument parameters for MS analysis of the mercapturic acid product was determined. Recovery studies using 10, 5, 1.25 and 0.61 $\mu\text{g/ml}$ PMA fortified human urine samples demonstrated good accuracy and precision with recoveries using the SPE procedure of between 93-102% with precision measured as percent relative standard deviation (%RSD) as high as 5.2%. This

biomarker was used for the evaluation of 1-BP exposure at numerous field sites. The solid phase extraction procedure was amenable to robotic automation which was less labor intensive and demonstrated better precision than manual sample preparation. PMA analysis appears to be a useful biomarker for the evaluation of 1-BP exposure.

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The National Institute for Occupational Safety and Health (NIOSH) and the Karolinska Institutet in cooperation with the Stockholm County Council are taking the lead in organizing this conference. NIOSH is maintaining this website.

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This conference follows the success of the first [International Conference on Occupational and Environmental Exposures of Skin to Chemicals: Science and Policy](#), which was held near Washinton, DC, in September, 2002.

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The organizers of OEESC-2005 appreciate those organizations that supported the goals of this conference through financial or in-kind contributions. Contributions were used to pay the full or partial travel and conference registration costs of invited speakers and guests and to reduce the registration fees of attendees by paying part of the costs associated with such expenses as meeting room rental, poster display board rental, abstract book, breaks, reception and conference dinner.

The conference account is managed by Karolinska Institutet.

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