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SPECIATION OF URINARY ARSENIC INTO  
OCCUPATIONAL AND DIETARY COMPONENTS:  
METHODOLOGY ADAPTED TO ZEEMAN  
FLAME ASS APPLICATION

S.J. DOMVILLE, L. DERJARLAIS, E. MADSEN,  
Nerco Con Mine, Bag 2000, Yellowknife  
Northwest Territories, Canada X1A 2M1

Arsenic trioxide, a by-product of the ore roasting process once utilized in our gold milling operation, is currently refined through an Arsenic Reclamation Plant at Nerco Con Mine, Yellowknife, Northwest Territories, Canada. In the process of solubilization and crystallization, employees are exposed to arsenic, primarily through respiration and ingestion.

Arsenic exposure is monitored through the analysis of urine, the most reliable route of arsenic elimination. The biological monitoring program requires collection of urine both before and after exposure periods within the Plant. The focus of the program is on:

- i) Peak exposures, for short-term health concerns; and
- ii) "body burden" for long-term health concerns. Body burden is interpreted (within our program) as an upward shift in a worker's baseline urinary arsenic level after consecutive exposure periods (Figure 1.)

There are many sources for arsenic in urine, other than occupational exposure. Effective management of the biological monitoring program identified the need for urinary arsenic "speciation". The ability to differentiate occupational (or inorganic) arsenic from other sources, primarily seafood, was developed within the Environmental Services Laboratory at Nerco.

#### TOTAL URINARY ARSENIC (Figure 1.)

##### DIRECT

The greatest responsibility of the biological monitoring program is to report, on a daily basis, total urinary arsenic levels. This is achieved (no preparatory steps required) by Zeeman Flame AAS. Arsenic levels are reported in terms of creatinine output, ( $\mu\text{g As/gram creatinine}$ ) in order to reflect kidney function and total urine output.

##### TOTAL DIGEST

A complimentary method, using a rigorous oxidative digestion (sulfuric acid - persulfate) has now been developed. As well as a means of confirmation, this method provides improved precision and accuracy through the extraction of arsenic into a uniform matrix (nickelous nitrate).

#### OCCUPATIONAL (INORGANIC) ARSENIC ONLY (Figure 1.)

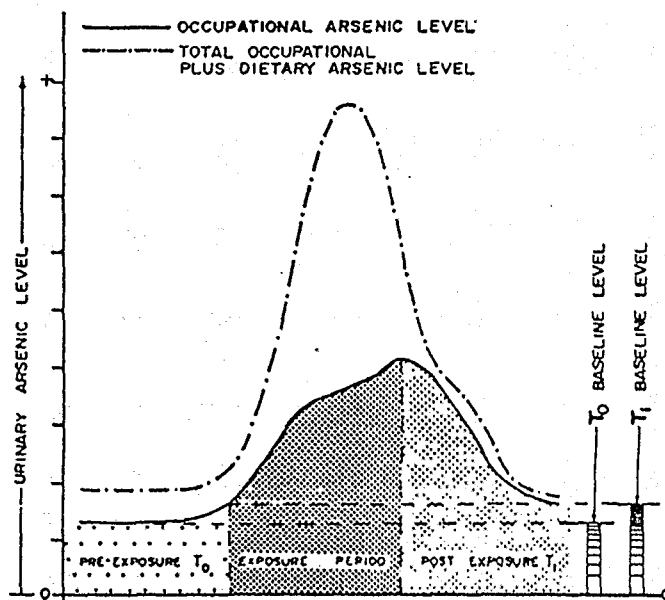
##### PARTIAL DIGEST

The "hydrolysable" arsenic fraction, representing occupational exposure, is differentiated from the "total" arsenic pool through an acid hydrolysis, potassium iodide reduction, solvent extraction, and back-extraction process. The dietary fraction, including arsenobetaine, is separated and removed at the solvent (toluene) extraction step. The monomethylarsonic acid and cacodylic acid species (methylated arsenic forms representing occupational exposure) are de-methylated through acid hydrolysis. Arsenic from these species is then reduced by potassium iodide, and extracted into toluene. Back-extraction into nickelous nitrate results in detection limits within the range of 30 - 50  $\mu\text{g As/Liter}$  of urine (using Zeeman Flame AAS).

Extensive quality control and interlaboratory comparison, for both "total" and "occupational" arsenic determinations, have provided employees of the Arsenic Reclamation Plant with a high level of confidence in our analytical performance and program management.

FIGURE 1.

#### URINARY ARSENIC SPECIATION



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