

MEDICAL SERVICES BRANCH

RECORDING & TRANSMITTAL FORM

MINISTER'S CORRESPONDENCE

SUBJECT:	Medical data obtained from urine tests	FILE NO: <u>850-5-X751</u>
FROM:	Mr. Wayne Bannick Chairman, Safety Committee United Steelworkers of America Local 802 Box 327 YELLOWKNIFE, Northwest Territories	DATE: <u>October 20 '75</u>
TO:	Minister	INITIATED IN BRANCH
<div style="display: flex; justify-content: space-between;"> <div> RECEIVED IN ADM'S OFFICE: <u>December 15 '75</u> (Date) </div> <div> PASSED: <u>December 15 '75</u> (Date) </div> </div>		
ACTION:	Please prepare a reply for the Executive Assistant's signature (Ann. C. Jamieson) by December 23 '75.	

TO	DATE	REPLY			B.F.	DATE SENT TO MINISTER	SIGNED
		INTERIM	FINAL	DATE			
Dr. Thomson	Dec. 15 '75		<i>Jat</i>	<i>19-12-75</i>			
<i>Anne</i>	<i>Dec 19</i>		<i>X</i>	<i>Dec 19</i>			
		<i>retape</i>	<i>X</i>	<i>Dec 23</i>			
<i>Anne</i>	<i>24/12</i>					<i>Dec 24 '75</i>	

REMARKS:



**UNITED STEELWORKERS OF AMERICA**

**LOCAL 802**

**BOX 327**

**YELLOWKNIFE N.W.T.**

850-5-X751  
Dept. of National Health & Welfare  
Minister's Office  
RECEIVED

DEC 8 1975

Ministère de la Santé Nationale et  
du bien être social, Cabinet du Ministre  
REÇU

October 20, 1975

Honourable Marc Lalonde  
Minister of National Health & Welfare  
House of Commons  
Ottawa, Ontario

Mr. Lalonde,

Our local union safety committee is studying the report on arsenic of your officials released in Ottawa and Yellowknife on October 3. We intend to take up the recommendations with the companies as soon as possible, although we suspect that without stronger laws to protect workers in dangerous jobs in the N.W.T. the companies will not comply.

We wonder whether you would consider releasing the medical data obtained from the urine tests used in this study. In the 1971 study ( by A. J. de Villers and P. M. Baker of your department's occupational division ) urine samples were also done and the results were released ( not by name of individual but by groups.)

For some reason the latest urine sample results have not been disclosed, and we think it would be useful to have such information. It would be helpful to know if the arsenic levels in the latest tests are higher than in the earlier study.

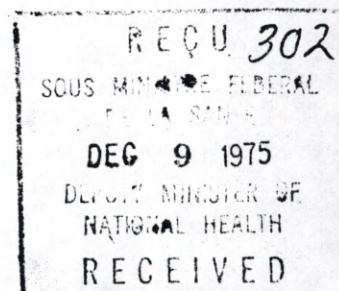
Thank you very much.

Yours truly,

*Wayne D. Bannick*

Wayne Bannick,  
Chairman, Safety Committee  
Local 802, U.S.W.A.

CC. Mr. W. Firth, M.P.  
Mr. H. L. Stevens  
Mr. W. Berezowski  
Mr. D. C. Wilson  
Mr. S. Hodgson







Medical Services Branch,  
370 Catherine Street,  
Ottawa, Ontario.  
K1A 0L3

July 30, 1975

Your file    Votre référence  
151-1-M (N3)  
Our file    Notre référence  
C-15

Dr. R.D.P. Eaton,  
Medical Services,  
Northwest Territories Region,  
14th Floor Baker Centre,  
10025 - 106 Street,  
Edmonton, Alberta.  
T5J 1H2

Dear Dr. Eaton:

Reference our telephone conversation of this date concerning the urine arsenic analysis results.

I am sending you the following results and related information:

Table 1 - this table lists the analysis results as obtained from Bondar-Clegg laboratories. The analytical results in the table have not been corrected for specific gravity.

Table 2 - this table contains the urine arsenic results corrected for specific gravity according to the two methods recommended by NIOSH, namely, method 10.1.2 and 10.1.3. Please note that in the application of method 10.1.3 "...the use of such a correction factor can lead to unusually or erroneously high results."

On Page 246 of one of the latest issues of Occupational Safety and Health Reporter (also attached) an attempt was made to clarify this situation by proposing that all urine samples whose specific gravity was less than 1.010 be discarded on the basis of their unreliability. If this proposal were applied here, 19 of the urine samples would be unacceptable.

Attached for your information is a letter we received from Dr. H.E. Stokinger. You might be interested in his comments on the reliability of arsenic levels in hair and urine samples as measures of exposures.

Yours truly,

J.P. Farant,  
Chemist.



TABLE 1

## UNCORRECTED ANALYTICAL RESULTS

URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	SPECIFIC GRAVITY	MEASURED CONCENTRATION OF ARSENIC IN URINE ug/litre
50269	2480	1.008	4
270	1970	1.025	68
271		1.015	52
272	200	1.014	12
273	1510	1.011	38
274	2440	1.006	62
275	1850	1.005	64
276	1000	1.023	42
277	3030	1.004	22
278	1520	1.015	86
279	3040	1.003	52



URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	SPECIFIC GRAVITY	MEASURED CONCENTRATION OF ARSENIC IN URINE ug/litre
280	670	1.026	22
281	1340	1.015	82
DOB 5/2/11	1020	1.021	14
282	2340	1.004	2
283	965	1.018	48
284	3250	1.007	14
285	2100	1.004	16
286	1450	1.014	60
287	1100	1.011	2
290	1650	1.023	40



URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	SPECIFIC GRAVITY	MEASURED CONCENTRATION OF ARSENIC IN URINE ug/litre
291	2730	1.005	35
292	2050	1.008	140
293	2080	1.012	59
294	1070	1.024	59
295	1285	1.020	108
296	1310	1.011	60
297	570	1.022	54
298	1000	1.014	16
299	550	1.022	98
300	2500	1.006	34



URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	SPECIFIC GRAVITY	MEASURED CONCENTRATION OF ARSENIC IN URINE ug/litre
301	1120	1.022	56
302	2970	1.004	16
303	2080	1.010	46
304	1100	1.018	58
305	2300	1.004	26
306	2700	1.001	44
307	3800	1.002	10
308	1550	1.022	52
309	1600	1.005	44
310	3400	1.004	36



URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	SPECIFIC GRAVITY	MEASURED CONCENTRATION OF ARSENIC IN URINE ug/litre
50311	900	1.017	80
312	950	1.019	102
313	2000	1.006	14
314	900	1.021	<2
315	900	1.019	198
316	850	1.021	68
317	1400	1.018	26
318	1500	1.018	38
319	1650	1.013	6
320	500	1.027	32
321	1100	1.013	16



URINE SAMPLE NUMBER
50322
323
324
325
326
327
328
329

VOLUME OF URINE/24 HRS. millilitres
2000
1350
1500
500
1000
1300
1550

SPECIFIC GRAVITY	MEASURED CONCENTRATION OF ARSENIC IN URINE ug/litre
1.013	16
1.008	156
1.012	20
1.010	40
1.016	36
1.016	56
1.017	88
1.016	38



TABLE 2

## ANALYTICAL RESULTS CORRECTED FOR SPECIFIC GRAVITY

URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	CONCENTRATION OF ARSENIC IN URINE ug/litre	
		METHOD 1	METHOD 2
50269	2480	4	12
270	1970	68	65
271		53	83
272	200	12	21
273	1510	39	83
274	2440	63	248
275	1850	65	307
276	1000	42	44
277	3030	22	132
278	1520	87	138



URINE SAMPLE NUMBER
---------------------------

VOLUME OF URINE/24 HRS. millilitres
---

CONCENTRATION OF ARSENIC IN URINE. ug/litre	
METHOD 1	METHOD 2

50282

2340

2

12

283

965

48

64

284

3250

14

48

285

2100

16

96

286

1450

61

103

287

1100

2

4

290

1650

40

42

291

2730

36

190

292

2050

142

419

293

2080

60

118



URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	CONCENTRATION OF ARSENIC IN URINE ug/litre	
		METHOD 1	METHOD 2
50294	1070	59	59
295	1285	109	134
296	1310	61	138
297	570	54	60
298	1000	16	27
299	550	98	107
300	2500	35	81
301	1120	56	61
302	2970	16	96
303	2080	47	110



URINE SAMPLE NUMBER
50304
305
306
307
308
309
310
311
312
313

VOLUME OF URINE/24 HRS. millilitres
1100
2300
2700
3800
1550
1600
3400
900
950
2000

CONCENTRATION OF ARSENIC IN URINE ug/litre	
METHOD 1	METHOD 2
58	77
27	156
45	1056
10	120
52	57
45	211
37	216
81	113
103	129
14	56



URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	CONCENTRATION OF ARSENIC IN URINE ug/litre	
		METHOD 1	METHOD "
50314	900	< 2	< 2
315	900	199	250
316	850	68	78
317	1400	26	35
318	1500	38	51
319	1650	6	11
320	500	32	28
321	1100	16	21
322		16	30
323	2000	158	468



URINE SAMPLE NUMBER	VOLUME OF URINE/24 HRS. millilitres	CONCENTRATION OF ARSENIC IN URINE ug/litre	
		METHOD 1	METHOD 2
324	1350	20	40
325	1500	41	96
326	500	36	54
327	1000	56	84
328	1300	89	124
329	1550	38	57
279	3040	53	416
280	670	22	20
281	1340	83	131

DOB-8-2-11

1025



NIOSH  
MANUAL OF ANALYTICAL METHODS

Physical and Chemical Analysis Branch  
Division of Laboratories and Criteria Development  
1014 Broadway, Cincinnati, Ohio 45202

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
Public Health Service  
Center for Disease Control  
National Institute for Occupational Safety and Health  
1974



10.1 The concentration of arsenic in the urine sample can be expressed as mg As per liter of urine.

$$\text{mg As/l} = \frac{\mu\text{g As}}{\text{mL of urine}} \quad (\text{from calibration curve, Section 9.2})$$

10.1.1 The use of a specific gravity correction factor to normalize values to 1.024, the average specific gravity of urine, has been proposed. There are two ways of using this correction.

10.1.2 One way is to use a straightforward gravity correction, in which case the magnitude of the factor is small.

Method 1

$$\text{corrected mg As/l} = \text{mg As/l} \times \frac{1.024}{\text{specific gravity}}$$

10.1.3 The other method corrects for differences in total solids or salt content of various urine specimens, whereby the specific gravity of water is initially subtracted from the urine specific gravities. Because of the wide range of reported urine specific gravities, 1.002 to 1.040, the use of such a correction factor can lead to unusually or erroneously high results.

Method 2

$$\text{corrected mg As/l} = \text{mg As/l} \times \frac{(1.024 - 1.000)}{(\text{specific gravity} - 1.000)}$$

10.2 The concentration of arsenic in air can be expressed as mg As per cubic meter of air, which is numerically equal to micrograms As per liter of air.

$$\text{mg As/m}^3 = \mu\text{g As/V}_s$$

where:

$\mu\text{g As}$  = micrograms As from calibration curve (Section 9.2)

$V_s$  = volume of air sampled in l at 25°C and 760 mm Hg.

## 11. References

11.1 Atomic Absorption Analytical Method No. As-3, Jarrell-Ash Co.

11.2 Atomic Absorption Application Study No. 468, The Perkin-Elmer Corp., June 1971.

11.3 Fernandez, Frank, J., "Atomic Absorption Determination of Gaseous Hydrides Utilizing Sodium Borohydride Reduction," Atomic Absorption Newsletter, 12, 93-97 (1973).



Henry V. Vaccaro Corporation, Neptune, N.J., is contesting a \$550 penalty for a serious citation for 1926.500 (b) (1) for failure to guard floor openings (No. 13755).

Village Blacksmith, Ingram, Tex., is contesting a six-item nonserious citation and a \$60 penalty, including 1910.215 (a) (4) for failure to provide workrests on grinders, 1910.252 (e) (2) (iii) for failure to provide flameproof screens or shields, and 1910.215 (a) (2) for failure to guard grinders (No. 13825).

Westinghouse Electric Corporation, Muncie, Ind., is contesting a nonserious citation for 1910.94 (c) (2) for failure to confine flammable or combustible spray finishing operations and 1910.252 (e) (2) (iii) for failure to provide protection from arc welding rays (No. 13790).

Westinghouse Electric Corporation, East Pittsburgh, Pa., is contesting a seven-item nonserious citation and a \$950 penalty, including 1910.107 (c) (6) for failure to provide suitable electrical wiring in a spraying area, 1910.107 (g) (7) for failure to post "no smoking" signs, and 1910.134 (b) (1) for failure to provide written procedures for the use and selection of respirators (No. 13800).

West Personnel, Inc., Oak Brook, Ill., is contesting a nonserious citation and a \$50 penalty for 1903.2 for failure to post an OSHA notice (No. 13826).

Williams Press, Inc., Menands, N.Y., is contesting a nonserious citation and a \$35 penalty for 1910.212 (a) (1) for failure to guard an inserting machine (No. 13793).

H. B. Zachry Company, San Antonio, Tex., is contesting a nonserious citation for 1926.651 (s) for failure to provide stops or barricades for mobile equipment (No. 13765).

## ABATEMENT PETITIONS

Century Drilling Company, Shelby, Mont., is requesting a 60-day extension of abatement from July 3, 1975, to provide adequate toilet facilities (No. 13792).

Dusquesno Light Company, Pittsburgh, Pa., is requesting an unspecified extension of abatement to guard a runway and mark exits adequately (No. 13357).

Hardy Salt Company, Williston, N.D., is requesting an extension of abatement from June 30, 1975 to August 31, 1975, to provide a fire alarm system (No. 13713).

Morse Electro Products Corporation, Brooklyn, N.Y., is requesting an unspecified extension of abatement from July 13, 1975, to correct six nonserious violations, including indicating direction of travel to the nearest exit, providing suitable clamp-on portable handlamps, and grounding electrical equipment (No. 13785).

T and B Foundry Company, Cleveland, Ohio, is requesting an unspecified extension of abatement from July 27, 1975, to reduce noise (No. 13850).

Williams Press, Inc., Menands, N.Y., is requesting a 30-day extension of abatement from July 3, 1975, to guard open-sided platforms and machinery (No. 13793).



Full Text

## NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH NEW CRITERIA FOR REGULATING OCCUPATIONAL EXPOSURE TO INORGANIC ARSENIC

### I. RECOMMENDATIONS FOR AN INORGANIC ARSENIC STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to arsenic and its inorganic compounds be controlled by requiring compliance with the following sections. The standard is designed to protect the health and safety of workers for a 40-hour week over a working lifetime. Compliance with all sections of the standard will prevent noncarcinogenic adverse effects of exposure to inorganic arsenic in the workplace air and by skin exposure, and should at the minimum materially reduce the risk of arsenic-induced cancer. The standard will be subject to review and will be revised as necessary.

"Arsenic" is defined as elemental arsenic and all of its inorganic compounds. "Exposure to arsenic" is defined as exposure at or above 0.002 mg (2.0 ug) As/cu m. Arsine and other arsenical gases should be controlled to the same concentration as other forms of inorganic arsenic. Suitable sampling and analytical methods for arsenical gases are not yet available but are being developed.

### Section 1 — Environmental (Workplace air)

#### (a) Concentration

Inorganic arsenic shall be controlled so that no worker is exposed to a concentration of arsenic in excess of 0.002 mg (2.0 ug) per cubic meter of air as determined by a 15-minute sampling period.

#### (b) Sampling and Analysis

Procedures for sampling, calibration of equipment, and analysis of arsenic samples shall be as provided in Appendices I and II, or by any method shown to be equivalent in precision, accuracy, and sensitivity to the methods specified.

### Section 2 — Medical

Medical surveillance shall be made available and related records kept as specified below for all workers occupationally exposed to arsenic.

(a) Preplacement and annual medical examinations shall include:



(1) Comprehensive preplacement or annual interim work history.

(2) Comprehensive preplacement or annual interim medical history.

(3) 14 inches x 17 inches posterior-anterior chest X-ray, giving particular attention to parenchymal and hilar changes.

(4) Careful examination of the skin to detect the presence of arsenic-induced hyperpigmentation, keratoses, or other chronic skin lesions. Skin examinations shall be repeated bimonthly if arsenic-induced skin lesions are detected. Care shall be taken to observe and record the location, condition, appearance, size, and any changes in all such lesions.

(5) Palpation of superficial lymph nodes to detect indications of neoplastic changes.

(6) Complete blood count to include differential.

(7) An evaluation of the advisability of the worker's using negative- or positive-pressure respirators.

(b) A periodic sputum cytology examination is recommended for all workers occupationally exposed to inorganic arsenic. The frequency of this procedure should be determined by the responsible medical authority.

(c) Proper medical management shall be provided for workers adversely affected by occupational exposure to inorganic arsenic compounds.

(d) Initial annual examinations for presently employed workers shall be offered within 6 months of the promulgation of a standard incorporating these recommendations.

(e) The medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, and of the employer shall have access to all pertinent occupational medical records. Physicians designated and authorized by any employee or former employee shall have access to that worker's medical records.

(f) Medical records shall be maintained by the employer or successors thereto for persons employed one or more years in work involving exposure to arsenic. Preplacement X-rays, X-rays for the 5 years preceding termination of employment, and all other medical records with pertinent supporting documents shall be maintained at least 30 years after the individual's employment is terminated. In the event that the employer ceases business without a successor, records shall be forwarded by registered mail to the Director, National Institute for Occupational Safety and Health.

### Section 3 — Labeling (Posting)

(a) Containers of arsenic compounds shall bear the following label in addition to or in combination with labels required by other statutes, regulations, or ordinances.

NAME OF COMPOUND  
DANGER! CONTAINS ARSENIC  
CANCER CAUSING AGENT

HARMFUL IF INHALED OR SWALLOWED, OR UPON  
SKIN CONTACT

AVOID CONTACT WITH SKIN, EYES, AND CLOTHING  
WASH THOROUGHLY AFTER HANDLING

Avoid breathing dust or spray mist

Keep container closed

Use only with adequate ventilation

(b) The following warning sign shall be affixed in a readily visible location at or near entrances to areas in which there occupational exposure to arsenic.

ARSENIC  
DANGER! CANCER CAUSING AGENT

Dust or spray mist may be hazardous to health

Provide adequate ventilation

This sign shall be printed both in English and in the predominant language of non-English workers unless they are otherwise trained and informed of the hazardous area. All illiterate workers shall receive such training.

### Section 4 — Personal Protective Equipment and Work Clothing

#### (a) Protective Clothing

(1) Where there is occupational exposure to inorganic arsenic compounds, protective clothing shall be provided by the employer. This may include underwear, gloves, coveralls, and a hood over the head and neck. When liquids are being processed in a manner that may result in splashes, impervious gloves, aprons, and splash goggles shall be used.

(2) Protective clothing shall be changed at least daily at the end of the shift.

(3) Work clothing shall not be taken home by employees. The employer shall provide for maintenance and laundering of protective clothing.

(4) The employer shall ensure that precautions necessary to protect laundry personnel are observed when soiled protective clothing is laundered.

#### (b) Respiratory Protection

(1) Engineering controls shall be used wherever feasible to maintain arsenic concentrations below the prescribed limit. Compliance with the permissible exposure limit may not be achieved by the use of respirators except:

(A) During the time period necessary to install or test the required engineering controls.

(B) For nonroutine operations such as a brief exposure to concentrations in excess of the permissible exposure limit as a result of maintenance or repair activities.

(C) During emergencies when air concentrations of arsenic may exceed the permissible limit.

(2) When a respirator is permitted by paragraph (b) (1) of this Section, it shall be selected and used pursuant to the following requirements:

(A) The employer shall ensure that no worker is being exposed to arsenic in excess of the environmental limit because of improper respirator selection, fit, use, or maintenance.

(B) A respiratory protection program meeting the requirements of 29 CFR 1910.134 as amended shall be established and enforced by the employer.

(c) The employer shall provide respirators in accordance with Table I-1 below and shall ensure that the employee uses the respirator provided.

(D) Respiratory protective devices described in Table I-1 shall be those approved under the provisions of 30 CFR 11 as amended.

(E) The employer shall ensure that respirators are adequately cleaned, and that employees are instructed in the use of respirators assigned to them, and how to test for leakage.

(F) Where an emergency may develop which could result in employee exposure to arsenic, the employer shall provide respiratory protection as listed in Table I-1.

TABLE I-1

(1) Combination supplied air respirator, pressure demand type, with auxiliary self-contained air supply.

(2) Self-contained breathing apparatus with positive pressure in the facepiece

### Section 5 — Informing Employees of Hazards from Inorganic Arsenic

At the beginning of employment in an arsenic area, employees exposed to arsenic compounds shall be informed



of the hazards, relevant symptoms of overexposure, appropriate emergency procedures, and proper conditions and cautions for safe use. Instruction shall include, as a minimum, all information in Appendix III which is applicable to the specific arsenic-containing product or material to which there is exposure. The information shall be posted in the work area and kept on file and readily accessible to the worker at all places of employment where arsenic is involved in unit processes and operations.

A continuing educational program shall be instituted to ensure that all workers have current knowledge of job hazards, proper maintenance procedures and cleanup methods, and that they know how to correctly use respiratory protective equipment and protective clothing.

Information as required shall be recorded on the "Material Safety Data Sheet" shown in Appendix III or on a similar form approved by the Occupational Safety and Health Administration, U.S. Department of Labor.

### Section 6 — Work Practices

(a) Readily accessible standby rooms under positive air pressure and in which the concentration of arsenic in the air is less than 2.0 ug As/cu m shall be provided where there is occupational exposure to inorganic arsenic.

(b) Arsenic shall be removed from work areas by vacuum cleaning or wet methods. Cleaning may be performed by washing down with a hose, provided that a fine spray of water has first been laid down. Sweeping or other methods which can stir the dust into the air shall not be used.

(c) Waste material shall be disposed of in a manner which will prevent exposure of humans and animals as well as air and water pollution.

(d) Arsenic trichloride shall be handled only in enclosed systems sufficient to prevent skin contact and to prevent worker exposure in excess of the environmental limit.

(e) Where there is possibility of arsenic trichloride contact with the skin, emergency showers shall be provided in readily accessible locations. Eye-wash facilities shall also be conveniently located.

(f) Procedures for emergencies, including fire fighting, shall be established to meet foreseeable events. Necessary emergency equipment, including appropriate respiratory protective devices, shall be kept in readily accessible locations. Only self-contained breathing apparatus with positive pressure in the facepiece shall be used for fire fighting. Appropriate respirators should also be available for use during evacuation.

(g) Exhaust ventilation and enclosure of processes shall be used wherever practicable control workplace concentrations.

(h) Air from the exhaust ventilation system shall not be recirculated into work areas, and necessary measures shall be taken to ensure that discharge outdoors will not produce a health hazard to humans or animals.

(i) Due to potential skin irritation associated with respirator use and arsenic dust exposure, workmen shall be permitted to leave the work area every 2 hours to wash their face and obtain a clean respirator.

### Section 7 — Sanitation Practices

(a) Employees exposed to arsenic shall be provided with separate lockers or other storage facilities for street clothes and for work clothes.

(b) Employees exposed to arsenic shall not wear work clothing away from the plant.

(c) Facilities for shower baths shall be provided for employees exposed to arsenic. Workers shall shower bathe

before changing into street clothes. Shower baths shall be cleaned following use after each work shift.

(d) Employees exposed to arsenic shall wash their hands and exposed skin before eating or smoking during the work shift.

(e) No food shall be permitted in areas where arsenic is handled, processed, or stored.

(f) Employees shall not smoke in areas where arsenic is handled, processed, or stored.

### Section 8 — Monitoring and Recordkeeping

Workroom areas shall not be considered to have arsenic exposure if environmental levels, as determined on the basis of a professional industrial hygiene survey, are less than 2.0 ug As/cu m. Records of these surveys, including the basis for concluding that air levels are less than 2.0 ug As/cu m, shall be maintained in accordance with Section 8 (e). In workrooms where inorganic arsenic compounds are handled or processed, surveys shall be repeated at least annually and when any process change indicates a need for reevaluation. Requirements set forth below apply to areas in which 1 or more 15-minute breathing zone samples have indicated exposure at or above 2.0 ug As/cu m.

Employers shall maintain records of environmental exposures to arsenic based upon the following sampling and recording schedules:

(a) In all monitoring, sufficient breathing zone samples shall be collected to characterize the potential exposure of workers at each operation or process.

(b) The first environmental sampling shall be completed within 6 months of the promulgation of a standard incorporating these recommendations.

(c) Environmental samples shall be taken within 30 days after first operation of a new process or process changes.

(d) Samples shall be collected at least every 2 months for those work areas in which there is occupational exposure to inorganic arsenic.

(e) Records of all sampling and of medical examinations shall be maintained by the employer or successors thereto, for at least 30 years after the individual's employment is terminated. Records shall indicate the type of personal protective devices, if any, in use at the time of sampling. Records shall be maintained so that exposure information is available for individual employees, and each employee shall be able to obtain information on his own exposure. In the event that the employer ceases business without a successor, records shall be forwarded by registered mail to the Director, National Institute for Occupational Safety and Health.

## VII. APPENDIX I AIR SAMPLING PRACTICES FOR ARSENIC

### General Requirements

In order to evaluate conformance with the standard, 15-minute breathing zone samples representative of the individual worker's exposure shall be collected. Sampling data sheets shall include:

- The date and time of sample collection
- Sampling duration
- Volumetric flowrate of sampling
- A description of the sampling location
- Other pertinent information

### Air Sampling

(a) Fifteen-minute breathing zone samples representative of worker exposure shall be collected to characterize the exposure from each job or specific operation in each production area.



(b) Samples shall be collected using a portable sampling pump with a cellulose membrane filter with a pore size of 5.0  $\mu$ m or less mounted with backup pad in a 2- or 3-piece closed cassette.

(c) The sampler shall be operated at a flowrate of 2 liters/min and samples taken for 15 minutes.

(d) A minimum of 3 samples shall be taken for each operation or process.

(e) For 20 or fewer samples, 3 blank filters carried in closed cassettes to the sampling site shall be provided to the analytical laboratory for determination of the background correction which must be applied to the analytical results. One additional blank shall be provided for each 10 samples after the first 20.

#### Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential for the correct interpretation of the volume indicated. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been subjected to misuse or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a 1- or 2-liter buret or wet fit meter is recommended, although other standard calibrating instruments such as spirometer, Marriott's bottle, or dry-gas meter can be used.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a cellulose membrane filter is shown in Figure X-1. Since the flowrate given by a pump is dependent on the pressure drop of the sampling device, in this case a membrane filter, the pump must be calibrated while operating with a representative filter and backup pad in line.

(1) While the pump is running, the voltage of the pump battery is checked with a voltmeter to assure adequate voltage for calibration. The battery is charged if necessary.

(2) Place the cellulose membrane filter with backup pad in the filter cassette.

(3) The sampling train is assembled as shown in Figure X-1.

(4) The pump is turned on and the inside of the soapbubble meter is moistened by immersing the buret in the soap solution and drawing bubbles up the inside until they are able to travel the entire buret length without bursting.

(5) The pump rotameter is adjusted to provide a flowrate of 2.0 liters/min.

(6) The water manometer is checked to insure that the pressure drop across the sampling train does not exceed 13 inches of water at 2 liters/min.

(7) A soapbubble is started up the buret and the time it takes the bubble to transit a minimum of 1.0 liter is measured with a stopwatch.

(8) The procedure in (7) above is repeated at least 3 times, the results averaged, and the flowrate calculated by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(9) Data for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

## VII. APPENDIX II ANALYTICAL METHOD FOR ARSENIC IN URINE AND AIR

### PRINCIPLE OF METHOD

Samples are ashed with a mixture of nitric, perchloric, and sulfuric acids to destroy the organic matrix, and taken to fumes of sulfur trioxide to ensure that all traces of nitric acid are removed. The sample is transferred to an arsine generator where the arsenic is converted to the trivalent form. The arsine is generated from the sample either by the addition of metallic zinc or by the addition of sodium borohydride. The arsine is flushed through the burner of an atomic absorption spectrophotometer for the determination of arsenic content.

### RANGE AND SENSITIVITY

For a 25-ml urine sample, the range extends from 0.001 to 0.040 mg As/liter. The range can be extended by taking smaller (or larger) aliquots for analysis. For a 30-liter air sample, the range extends from 0.001 to 0.060 mg As/cu m. Fernandez [86] reported an absolute sensitivity of 0.005  $\mu$ g (5.0 ng) of arsenic using sodium borohydride reduction, a balloon collection technique, and an electrodeless discharge arsenic lamp.

### INTERFERENCES

Organic arsenic compounds would cause a positive interference. Appropriate background correction techniques must be applied in order to eliminate nonspecific absorption at 1937 Å.

### PRECISION AND ACCURACY

At the 95% confidence level, the precision of the atomic absorption method using a continuous flow system is 9% for 1.0  $\mu$ g As/sample, and is 25% for 0.10  $\mu$ g As/sample. NIOSH calculated these values from 15 data points, each obtained over several independent runs. The precision of the present balloon technique may be different.

Fernandez [86] reported a coefficient of variation of 3.2% for 0.25  $\mu$ g As/sample using the balloon collection method. However, the coefficient of variation at the recommended standard (0.050  $\mu$ g or 60.0 ng As/sample) is expected to be greater.

The accuracy of the method has not been determined at this time.

### ADVANTAGES AND DISADVANTAGES OF THE METHOD

This method has the advantage of being free of interference by antimony. It is somewhat faster, and several times as sensitive as the colorimetric method for arsenic. The disadvantages include the requirement of specialized equipment and the use of rather large volumes of expensive gases. This analytical procedure does not distinguish between pentavalent and trivalent arsenic compounds. Specialized research methods which are not widely used reportedly can distinguish between these valence states. [110, 111]

### APPARATUS

(a) Atomic absorption spectrophotometer equipped with arsine generator, deuterium arc background correction, and



argon-hydrogen system. (Figure X-2) An electrodeless discharge arsenic lamp is recommended.

- (b) 125-ml borosilicate Phillips beakers.
- (c) Good facilities capable of handling perchloric acid fumes.
- (d) Specific gravity meter or hydrometer capable of measuring specific gravities in the range of 1.000-1.040 plus or minus 0.001.
- (e) 25-ml borosilicate volumetric flasks.

## REAGENTS AND GASES

All chemicals must be ACS reagent grade or better. Double deionized water or equivalent must be used.

- (a) Nitric acid, distilled reagent grade.
- (b) Perchloric acid, 72%.
- (c) Sulfuric acid, 90%.
- (d) Hydrochloric acid, 36%.
- (e) Potassium iodide solution. Dissolve 20 g of potassium iodide in 100 ml double distilled water.
- (f) Stannous chloride solution. Dissolve 20 g of stannous chloride dihydrate in 100 ml of concentrated hydrochloric acid.
- (g) Zinc, 20 mesh granular, low arsenic.
- (h) Sodium borohydride, 11/32-inch pellets.
- (i) Arsenic standard stock solution, 1,000 ppm. Dissolve 1.320 g of arsenic trioxide in 10 ml of 40% sodium hydroxide and dilute to 1 liter with distilled water. Commercially prepared stock solutions are also available. Working standards are made by diluting the stock solution.
- (j) Gases. Hydrogen, electrolytic grade. Argon, high purity.

## PROCEDURE

### (a) Cleaning Equipment

All glassware must be cleaned with a detergent solution followed by both tap water and distilled water rinses. Then the glassware is cleaned with hot concentrated nitric acid and thoroughly rinsed with tap water followed by distilled water. (Arsine generators are rinsed with concentrated hydrochloric acid following the nitric acid wash.)

### (b) Collection of Urine Samples

Urine samples are collected in polyethylene bottles which are precleaned in nitric acid. About 0.1 g EDTA is added as a preservative. At least 75 ml of urine should be collected. Care should be taken to prevent leaking of bottles in transit.

### (c) Collection of Air Samples

Air samples are collected in accordance with Appendix I.

## ANALYSIS OF SAMPLES

Determine the specific gravity of the urine sample at room temperature. This may be done with the use of a specific gravity meter or a reliable hydrometer.

Transfer 25 ml of the urine sample, or the membrane filter for air samples, into a 125-ml Phillips beaker. Wet-ash the sample by treating with 5 ml of a mixture of 3 parts nitric acid, 1 part sulfuric acid, and 1 part perchloric acid and heating on a hot plate at 130-150 C. Keep adding small amounts of redistilled nitric acid until a colorless (liquid) ash is obtained. If the ashing is still incomplete, additional perchloric acid can be added dropwise. Continue heating to fumes of sulfur trioxide.

Allow the mixture of cool, then transfer to a 25-ml volumetric flask and make up to volume with distilled water. For urine samples, pipet a 5-ml aliquot of the 25-ml sample into an arsine generation flask with balloon attached. For air

samples, transfer the entire sample to the arsine generation flask. The arsine can be generated by either of the following 2 methods.

(a) Reduction with zinc. Add in order 15 ml of distilled water, 10 ml of concentrated hydrochloric acid, 2 ml of potassium iodide solution, and 2 ml of stannous chloride solution. (Swirl solution after the addition of each reagent for homogeneous mixing.) Mix well and allow to stand for 15 minutes to insure the conversion of arsenic to the trivalent form. Attach the flask to the generating system and open the 4-way stopcock for 15 seconds to flush the air out of the system with argon. Add 1.5 g of zinc to the sample solution via the addition stopcock.

(b) Reduction with sodium borohydride. Add 35 ml of distilled water, 5 ml concentrated hydrochloric acid, and mix well. Connect the sample flask to the generating system and open the 4-way stopcock for 15 seconds to flush air out of the system with argon. Add to the sample solution, via the addition stopcock, a single sodium borohydride pellet (11/32-inch diameter, 200-mg).

The reaction is vigorous and the balloon fills with the evolved gases thus acting as a reservoir for the generating system. After one minute, open the 4-way stopcock allowing the pressure in the balloon to flush the gases into the flame of the atomic absorption instrument. The absorbance is recorded on a rapid response strip chart recorder. Larger (or smaller) aliquots of the sample solution may be taken if the signal is not in the proper range.

## CALIBRATION AND STANDARDS

Prepare working standards of 0.25, 0.50, 1.0, 3.0, 5.0, and 7.0 µg of arsenic in 25 milliliters of solution by dilution of the standard stock solution. These standards should be prepared fresh each time.

Construct a calibration curve by pipetting 5 ml of each of the working standards into arsine generators and proceeding with the analysis. A calibration curve of absorbance versus micrograms of arsenic is plotted and used for the determination of arsenic content of the samples.

## CALCULATIONS

### (a) Urine Samples

The concentration of arsenic in the urine sample can be expressed as mg As/liter of urine.

$$\text{mg As/liter} = \frac{\mu\text{g As}}{\text{ml of urine}} \quad (\text{from calibration curve})$$

The use of a specific gravity correction factor to normalize values to 1.024, the average specific gravity of urine, has been proposed. [92-94, 96] The following correction is recommended. Specific gravities less than 1.010 are unreliable and these samples should be discarded.

$$\text{corrected mg As/liter} = \text{mg As/liter} \times \frac{(1.024 - 1.000)}{(\text{specific gravity} - 1.000)}$$

### (b) Air Samples

The concentration of arsenic in air can be expressed as milligrams As per cubic meter of air, which is numerically equal to micrograms As per liter of air.

$$\text{mg As/cu m} = \mu\text{g As/l}$$

where:

$$\mu\text{g As} = \text{micrograms As from calibration curve}$$

$$V = \text{volume of air sampled (in liters) at 25 C and 760 mmHg.}$$



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June 17, 1975

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Mr. C. R. Ross, P. Eng.  
Consultant, Occupational Environments  
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370 Catherine Street  
Ottawa, Ontario, Canada K1A-0L3

Dear Mr. Ross:

In response to your letter of June 11 requesting documentation for the TLV for ARSENIC, we are pleased to enclose a copy of the documentation for Arsenic Trioxide Handling and Use and one for Arsenic Trioxide Production.

The distinction of the separate industrial air standards was made on the basis that different types of exposure occur under different conditions of industrial operations, requiring, according to a new policy established by the Threshold Limits Committee, the tailoring of the industrial air standard (TLV) to the particular industrial operation.

This is in distinct contrast to the NIOSH recommendation for inorganic arsenic. NIOSH's Criteria Document on Inorganic Arsenic makes a blanket air standard for all inorganic compounds of arsenic, and, furthermore, is proposing in a document yet to appear, an unrealistically low level of  $2 \mu\text{g}/\text{m}^3$  as arsenic.

\*\*\*

Thank you for sending on the copy of your recent results of arsenic levels in the hair of residents in Yellowknife. They seem to bear out very well the degree of exposure of mine and mill workers vs. other residents of Yellowknife.

We might, however, offer a word of caution in the use of hair analyses as a measure of trace metal exposure, particularly in the case of arsenic, which, as you know, is a ubiquitous element occurring in many dietary items. In connection with this, we had occasion to analyze the nails of a number of our staff here some time ago for their arsenic contents. To everyone's surprise, the arsenic content of the nails of my wife was approximately 100 times the



Page 2 - Mr. C. R. Ross

average of the workers in our facility here and that of mine was more than 130 times the average. Neither of us, to our knowledge, had any peculiar exposure to arsenic other than dietary, possible contributors being wines and seafood. On analyzing our nail specimens a few months later, the arsenic content had gone down respectively to 17 and 30 times normal. During this period and to date, we have been in perfect health these many years (my wife is a physician).

What we make of these fluctuating arsenic levels in dermal appendages is that unless the dietary intake of arsenic is uniform, all sorts of unexplained levels can occur, and urinary values are of no use as a measure of exposure unless a method is developed, which has not yet been done, to separate organically bound arsenic from inorganic arsenic.

Sincerely yours,

A handwritten signature in cursive script that reads "H. E. Stokinger".

Herbert E. Stokinger, Ph.D.  
Chairman  
Committee on Threshold Limits

2 Enclosures