

METALS in Urine

8310

TABLE 1

MW: Table 1

CAS: Table 1

RTECS: Table 1

METHOD: 8310, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to the following metals or their compounds: aluminum, barium, cadmium, chromium, copper, iron, lead, manganese, molybdenum, nickel, platinum, silver, strontium, tin, titanium, and zinc.

SYNONYMS: vary according to the compound

SAMPLING	MEASUREMENT
<p>SPECIMEN: urine</p> <p>VOLUME: 50 to 200 mL in polyethylene bottle</p> <p>PRESERVATIVE: 5.0 mL conc. HNO₃ added after collection</p> <p>SHIPMENT: frozen in dry ice</p> <p>STABILITY: not established</p> <p>CONTROLS: collect at least 3 urine specimens from unexposed workers</p>	<p>TECHNIQUE: INDUCTIVELY-COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)</p> <p>ANALYTE: elements above</p> <p>EXTRACTION MEDIA: polydithiocarbamate resin</p> <p>FINAL SOLUTION: 4% HNO₃, 1% HClO₄; 5 mL</p> <p>WAVELENGTH: depends upon element; Table 2</p> <p>BACKGROUND CORRECTION: spectral wavelength shift</p> <p>CALIBRATION: elements in 4% HNO₃, 1% HClO₄</p> <p>QUALITY CONTROL: spiked urines; corrected for creatinine</p> <p>RANGE: 0.25 to 200 µg per sample [1]</p> <p>ESTIMATED LOD: 0.1 µg per sample</p> <p>PRECISION (\hat{S}_r): Table 2</p> <p>ACCURACY: Table 2</p>

APPLICABILITY: This method measures urine concentrations of metals. It is particularly useful for workers exposed to several metals simultaneously. This is a simultaneous, multielemental analysis, but is not compound specific.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection and interelement correction factors. Background corrections are also made [1,2].

OTHER METHODS: This method uses a measurement technique similar to that of Method 7300 (Elements by ICP) for air samples.

REAGENTS:

1. Polydithiocarbamate resin, prepared as described in the APPENDIX.
2. Nitric acid, conc.*
3. Perchloric acid, conc.*
4. Dissolution acid, 4:1 (v/v) HNO₃:HClO₄. Mix 4 volumes conc. HNO₃ with 1 volume conc. HClO₄.*
5. Metals standards, 1000 µg/mL. Commercially available or prepared per instrument manufacturer's recommendations.
6. Argon.
7. Deionized water.
8. Sodium hydroxide, 5 M. Dissolve 20 g NaOH in 50 mL boiled, deionized water; dilute to 100 mL. Store in a polyethylene bottle.

* See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, 125- or 250-mL, plastic-lined screw-cap.**
2. Inductively-coupled plasma-atomic emission spectrometer equipped for determination of elements of interest.
3. Regulator, two-stage, for argon.
4. Filtering apparatus for 50 mL liquid with 47-mm cellulose ester, 0.8-µm pore size filters.
5. Beakers, Griffin, 50-mL, with watchglass covers.**
6. pH meter and electrodes.
7. Volumetric flasks, 5- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, suitable for use at 100 °C.
10. Mechanical shaker.
11. Low temperature oxygen plasma asher (acid ashing may be substituted; see Step 9).

** Clean all labware with detergent, soak 12 h in 10% (v/v) HNO₃, and soak 12 h in deionized water.

SPECIAL PRECAUTIONS: Concentrated acids are extremely corrosive. Work with concentrated acids only in fume hoods and wear appropriate safety equipment (safety glasses or face shield, gloves, and labcoat). Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

SAMPLING:

1. Collect a 50-mL urine sample in a polyethylene bottle.
2. Add 5 mL conc. HNO₃ as a preservative.
3. Pack samples in an insulated shipping container under refrigeration (e.g., styrofoam with dry ice) for transportation to laboratory.

SAMPLE PREPARATION:

4. Perform a creatinine determination on an aliquot of the sample (e.g., [3]).
5. Adjust the sample pH to 2.0 ± 0.1 with 5 M NaOH and then add 60 ± 10 mg polydithiocarbamate resin.
NOTE: Start reagent blanks, in triplicate, at this step. Include resin and filters (step 7).
6. Agitate samples (on the shaker) for at least 12 h.
7. Filter samples through a 0.8-µm cellulose ester membrane filter, saving the filtrate and resin. Place the collected resin and filter in a clean 50-mL beaker.
8. Adjust filtrate pH to 8.0 ± 0.1 with 5 M NaOH, add more resin, then repeat steps 5 and 6, combining the filters and resins from the two extractions.
9. Ash filters and resins in a low temperature oxygen plasma asher for 6 h or until ashing is

complete (200 watts at 1 to 2 torr, or manufacturer's recommendations).

NOTE: Steps 5 to 10 of Method 7300 (Elements by ICP), an $\text{HNO}_3/\text{HClO}_4$ digestion, may be substituted for the low temperature oxygen plasma ashing. Use a final solution volume of 5.0 mL (step 11).

10. Add 0.5 mL dissolution acid and warm on a hotplate (15 min at 50 °C).
11. Transfer solutions quantitatively to 5-mL volumetric flasks and dilute to volume with distilled deionized water.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to manufacturer's recommendations.
NOTE: Typically, an acid blank and 10 µg/mL multi-element solutions are used.
13. Analyze a standard for every 10 samples.
14. Check measurement recoveries with at least three spiked unexposed urine samples per 10 samples.

NOTE: For urine spikes, split a 100-mL control urine sample and analyze 50 mL without spiking. Subtract the metal quantity found in the unspiked portion from the metal quantity found in the spiked portion in order to determine measurement recovery.

MEASUREMENT:

15. Set the spectrometer to conditions specified by the manufacturer.
16. Analyze standards and samples.
NOTE: If the values for the samples are above the range of the standards, dilute the sample solutions with 1 volume dissolution acid plus 9 volumes deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentration for the sample, C_s (µg/mL), and the average blank, C_b (µg/mL), from the analyses data.
18. Using the solution volumes of sample, V_s (mL), and blank, V_b (mL), calculate the concentration, C (µg/mL), of each element in the volume of urine collected, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \text{ mg/m}^3.$$

19. Report the results as µg metal/g creatinine.

GUIDELINES TO INTERPRETATION:

Acceptable and unacceptable levels for metals have not been determined by this method. Lauwerys [4] discusses metals and can be consulted for guidance and interpretation.

EVALUATION OF METHOD:

Recovery of these 16 metals from spiked urine samples are shown in Table 2 (recoveries ranged from 77 to 100%). The precisions determined for the various elements are also given in Table 2 [1].

REFERENCES:

- [1] Hull, R. D. Analysis of Trace Metals for Occupationally Exposed Workers, Morbidity and Mortality Weekly Report, **33**, (1984).
- [2] Hull, R. D. ICP-AES Multi-element Analysis of Industrial Hygiene Samples, NTIS Publication No. PB85-221414, 1985.
- [3] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., pp. 994-997, W. B. Saunders Co., Philadelphia, PA (1976).
- [4] Lauwerys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA (1983).
- [5] Hackett, D. S. and S. Siggia. Selective Concentration and Determination of Trace Metals Using Polydithiocarbamate Chelating Ion-Exchange Resins, Environmental Analysis, p. 253, (G. W. Ewing, ed.), Academic Press, NY (1977).
- [6] Bray, J. T. and F. J. Reilly. Extraction of Fourteen Elements from a Sea Water Matrix by a Polydithiocarbamate Resin, Jarrell-Ash Plasma Newsletter, **4**, 4 (1981).

METHOD WRITTEN BY:

R. DeLon Hull, Ph.D., NIOSH/DBBS.

TABLE 1. GENERAL INFORMATION

Element (Formula)	Atomic Weight	CAS #	RTECS
Aluminum (Al)	26.98	7429-90-5	BD0330000
Barium (Ba)	137.34	7440-39-3	CQ8370000
Cadmium (Cd)	112.40	7440-43-9	EU9800000
Chromium (Cr)	52.00	7440-47-3	GB4200000
Copper (Cr)	63.54	7440-50-8	GL5325000
Iron (Fe)	55.85	7439-89-6	NO4565500
Lead (Pb)	207.19	7439-92-1	OF7525000
Manganese (Mn)	54.94	7439-96-5	OO9275000
Molybdenum (Mo)	95.94	7439-98-7	QA4680000
Nickel (Ni)	58.71	7440-02-0	QR5950000
Platinum (Pt)	195.09	7440-06-4	TP2160000
Silver (Ag)	107.87	7440-22-4	VW3500000
Strontium (Sr)	87.62	7440-24-6	
Tin (Sn)	118.69	7440-31-5	XP7320000
Titanium (Ti)	47.90	7440-32-6	XR1700000
Zinc (Zn)	65.37	7440-66-6	ZG8600000

TABLE 2. RECOVERY OF METALS FROM URINE [1,2]

Element (Formula)	Wavelength (nm)	Quantity Added, µg/50 mL sample	Precision, \bar{S}_r (n = 4)	Precision, % Recovery	Accuracy ± %
Aluminum (Al)	308.2	20	0.088	100	17.2
Barium (Ba)	455.4	0.4	0.11	80	41.6 ^a
Cadmium (Cd)	226.5	1.0	0.12	100	23.5
Chromium (Cr)	205.6	1.0	0.078	100	15.3
Copper (Cu)	324.8	10	0.042	100	8.2
Iron (Fe)	259.9	40	0.059	100	11.6
Lead (Pb)	220.4	10	0.040	100	7.8
Manganese (Mn)	257.6	10	0.50	85	113 ^a
Molybdenum (Mo)	281.6	2.0	0.16	100	31.4 ^a
Nickel (Ni)	231.6	2.0	0.42	80	102 ^a
Platinum (Pt)	203.7	0.4	0.29	77	79.8 ^a
Silver (Ag)	328.3	2.0	0.12	100	23.5
Strontium (Sr)	421.5	4.0	0.25	100	49.0 ^a
Tin (Sn)	190.0	2.0	0.21	100	41.2 ^a
Titanium (Ti)	334.9	2.0	0.16	86	45.4 ^a
Zinc (Zn)	213.9	200	0.089	100	17.4

^a Does not meet the NIOSH criterion of ± 25% accuracy.

APPENDIX: POLYDITHIOCARBAMATE RESIN PREPARATION

The procedure used for preparation of the polydithiocarbamate resin is that of Hackett and Siggia [5] as modified by Bary and Reilly [6].

1. Dissolve 72 g polyethyleneimine, molecular weight 1800, in 1 L tetrahydrofuran and 28 g polymethylenepolyphenyl isocyanate in 1 L tetrahydrofuran.
NOTE: Polyethyleneimine stored for one year would not dissolve in the solvent; however, fresh polyethyleneimine readily dissolved.
2. Pour these two solutions simultaneously into a large flask, allowing the two streams to mix before entering the flask.
3. Let the mixture stand at least 12 h with occasional mild agitation, then remove the solvent by filtration.
4. Wash the product twice with methanol and once with deionized water.
5. Add the product to 300 mL carbon disulfide, 100 mL ammonium hydroxide and 500 mL isopropyl alcohol; let stand 72 h.
6. Filter to remove the resin from the solvent mixture. Wash the resin three times with methanol and allow it to dry.
7. Grind and sieve the resin, saving the 60/80 mesh size for use.