The determination of mercury in whole blood and urine by inductively coupled plasma mass spectrometry

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Abstract

An inductively coupled mass spectrometric (ICP-MS) method for the determination of mercury in whole blood and urine was developed. Gold and dichromate in hydrochloric acid were evaluated as agents to reduce mercury spray chamber memory. Dichromate with hydrochloric acid was found to be superior to gold. We evaluated the rapid introduction of sample to promote equilibrium and the rapid introduction of wash solutions after the sample analyses to minimize mercury memory. This ‘fast pump’ mode (2.5 ml/min) was used for 20 s at the beginning and end of each sample-wash cycle. The mercury detection limit is 0.15 μg/l in the original sample before dilution. Regressions and correlation coefficients for ICP-MS vs. target concentrations for interlaboratory comparison samples from the Centre de Toxicologie du Quebec were: whole blood: \( y = 1.0x - 0.6; r = 0.9801; n = 27 \) and urine: \( y = 0.84x + 8; r = 0.9915; n = 42 \). Patient samples were analyzed by ICP-MS and cold vapor atomic absorption spectrometry (CVAAS). Regressions and correlations for patient samples were: urines: \( y = 0.93x + 1; r = 0.8763; n = 456 \) and whole blood: \( y = 1.1x + 0.2; r = 0.9357; n = 251 \). ICP-MS correlation with CVAAS for 29 urine samples containing 15–150 μg Hg/specimen was: \( y = 0.94x + 4; r = 0.9864 \). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The standard method for the determination of mercury in biomedical samples is cold vapor atomic absorption spectrometry (CVAAS) [1–9].

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After sample digestion or pretreatment to decompose organic mercury compounds, total mercury can be easily determined by stannous chloride reduction [4,5,7]. This method has been applied in a batch mode without digestion [3,4,8,9] and by flow-injection [5–7]. For effective analysis this method requires at least 500 μl of whole blood or 1000 μl of urine [7].

The method does have some limitations. The
The method used in our laboratory uses large amounts of strong acids and strong oxidants to assure the complete decomposition of organic mercury [7]. The sample preparation step is labor-intensive and time consuming. In addition, cysteine in urine samples or oxidizing agents such as iodine prevent the effective reduction of mercury by stannous chloride and the formation of nascent elemental mercury. Iodine can be present in urine after use as a radiological contract agent.

The potential advantages of inductively coupled plasma mass spectrometry (ICP-MS) for routine heavy metal screening are as follows: only 300 µl of urine and 150 µl of whole blood are required to perform the analysis [10]; essentially no sample preparation is required, only dilution with a diluent containing acid and internal standards. Significant savings in sample volumes, reagents, technician time and analysis time are realized.

Easy reduction of inorganic mercury to elemental mercury and the volatility of elemental mercury, prerequisites for effective CVAAS analysis, present major problems for the determination of mercury by ICP-MS. It is well known that after a sample containing mercury is nebulized into a conventional spray chamber, significant residual mercury signal can be detected many minutes afterwards. The mercury signal fails to return to baseline and all subsequent samples appear to contain mercury, whether they do or not. Retention of mercury in spray chambers and long washout times with nitric acid have been documented [11–13]. This phenomenon has been duplicated in our method development for ICP-MS heavy metal screening and the diluent containing acid and internal standards. Significant savings in sample volumes, reagents, technician time and analysis time are realized.

Several solutions to this problem of mercury spray chamber memory have been published. Flow injection and mercury reduction followed by gold amalgamation has been used to eliminate the aerosol spray chamber memory [17]. Mercury is subsequently released from the gold by heating and detected by ICPMS. Another solution is the direct injection nebulizer (DIN) [12]. This device also eliminated the spray chamber. Conventional spray chamber-pneumatic nebulization has been used with diluents such as tetramethyl ammonium hydroxide (TMAH) [14], ethylenediaminetetraacetic acid (EDTA) in TMAH [18], 25% HCl with cysteine [19], or gold [13,15,20] to modify samples to reduce the memory effect. Recently HBr has been used to reduce mercury memory in spray chambers [11]. All of these solutions appear to work but, for routine clinical applications, we favor the simple dilution approach coupled with conventional spray chamber-pneumatic nebulization. While the DIN appears to give excellent sensitivity with very small samples, clogging might present problems with whole blood samples. Certainly the flow injection-gold trap-ICP-MS method eliminates matrix effects and memory problems, but the method is as slow as CVAAS. The most viable and compatible methods with routine clinical analysis involve only simple dilution.

Our approach to the determination of mercury by simple dilution-pneumatic sample introduction is based on the knowledge that dichromate has been used as a modifier-oxidant for CVAAS [21] and graphite furnace mercury determination [22] and dichromate has also been effectively used as a preservative for mercury standard solutions [16]. When dichromate is present in solution, mercury titer does not change with time [16]. The addition of dichromate to acidified mercury standards prevents both the volatilization and adsorption losses of mercury [16]. Since dichromate is a strong oxidant, compounds such as mercurous sulfide (cinnabar) are completely solubilized and remain in solution [21]. With dichromate present, reduction of mercury to insoluble compounds such as Hg⁺ (calomel) or volatile Hg⁰ is prevented. In this paper we describe the use of dichromate in 2% HCl as a diluent for mercury analysis of whole blood and urine. HCl was chosen because initial trials with 1% HNO₃ showed that mercury
memory effects are severe. In addition HCl is effective for organic mercury solubilization [23] and total mercury determination by ICP-MS [19].

In addition to the combination of dichromate with HCl, gold was evaluated to determine if it is truly effective with biomedical samples. Gold was tried with and without added dichromate.

A rapid clearing spray chamber using a high volume wash solution combined with high volume gas flush has been designed to suppress matrix effects and increase sample throughput [24]. The liquid and gas flush combination reduced analyte signals for iron and copper over four orders of magnitude in less than 20 s [24].

The use of a high volume liquid flush alone was tried to help drive mercury from the spray chamber between samples. In this ‘fast pump’ mode a microprocessor was used to switch the sampling pump from normal 1 ml/min. to the ‘rabbit’ mode between samples. The spray chamber was purged with approximately 2.5 ml/min of diluent between samples.

Results for the ICPMS analysis of whole blood and urine were compared with our flow injection CVAAS method [9]. Commercially available quality control samples, interlaboratory comparison samples from the Centre de Toxicologie du Quebec, and patient samples were compared by both techniques.

2. Experimental

2.1. ICPMS facility

All ICP-MS experiments were performed on a Perkin-Elmer Sciex Elan 5000A instrument equipped with an AS-90 autosampler. Nickel sampler and skimmer cones were used for all experiments. Typical operating parameters are listed in Table 1. The mass flow controller for nebulizer gas flow, aerosol injector orifice position relative to the sampling cone, and mass spectrometer lens settings were adjusted on a weekly basis. Counts per second were maximized for Rh, Mg, and Pb by sequentially adjusting the above parameters while a solution containing 10 µg/l of each analyte in 1% HNO₃ was nebulized into the plasma. Typical counts for Rh after optimization were \(5 \times 10^4\) (counts \times 1)/s \times \text{mg}). Peak widths were also adjusted at the same time to maintain a 0.7 ± 0.1 amu peak width for \(^{103}\text{Rh}\) and a maxi-

<table>
<thead>
<tr>
<th>Instrument Conditions for the analysis of urine and whole blood for mercury</th>
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<tr>
<td><strong>Instrument</strong></td>
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<tr>
<td><strong>Power</strong></td>
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<tr>
<td><strong>Plasma gas flowrate</strong></td>
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<td><strong>Intermediate gas flowrate</strong></td>
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<td><strong>Nebulizer gas flowrate</strong></td>
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<td><strong>Nebulizer</strong></td>
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<td><strong>Spray chamber</strong></td>
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<td><strong>Resolution</strong></td>
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<td><strong>Isotopes</strong></td>
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<td><strong>Pb sum of 204(^b), 206, 207, 208</strong></td>
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<td><strong>Dwell time</strong></td>
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<td><strong>Mode</strong></td>
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<td><strong>Sample preparation</strong></td>
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<tr>
<td><strong>Diluent</strong></td>
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<tr>
<td><strong>Internal standard</strong></td>
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\(^a\)Nebulizer gas flow changes with optimization. 
\(^b\)Pb 204 corrected for Hg 204.
2.2. Isotopes

The sum of masses 198, 199, 200, 201, and 202 were used for mercury. Lead 204 corrected for mercury, 206, 207, and 208 were summed and used for memory effect comparisons. Bi 209 was used as the internal standard.

2.3. Reagents

Stock solutions of Hg, Pb, Au, and Bi were purchased from J.T. Baker Chemical Company (Phillipsburg, NJ) as Baker Instr-Analyzed Atomic Spectral Standards. Concentrations were nominally 1000 μg/ml except gold which was 500 μg/ml. GR Volumetric Grade K$_2$Cr$_2$O$_7$ and GR Grade hydrochloric acid was purchased from EM Science (480 S. Democrat Rd., Gibbstown, NJ). Reagent quality water was produced by processing laboratory-distilled water through a Barnstead NANOpure treatment system (Barnsted-Thermolyne; Dubuque, IA).

2.4. Laboratory ware

The following disposable laboratory items were used: Oxford pipette tips, no. 885-091341 (Monoject Scientific, Div. of Sherwood Medical, St. Louis, MO); polystyrene 75 × 12-mm 5-ml tubes (no. 55.476) and 6.0-ml screwcap vials (no. 61.542) (Sarstedt, Inc., Princeton, NJ). All items were used with no additional cleaning.

2.5. Certified controls

Specimens with pre-analyzed mercury concentrations were purchased from the National Institute of Standards and Technology; Gaithersburg, MD, USA (NIST-SRM 2670 toxic metals in freeze-dried urine; normal and elevated levels) and Bio-Rad, ECS Division, Anaheim, CA (Lyphochek urine metals control; level 2; two lots). Survey whole blood and urine samples were obtained by participation in Interlaboratory quality control program from the Centre de Toxicologie du Quebec.

2.6. Patient samples

Patient samples sequestered for method comparison were selected at random from an average of more than 30 urine specimens and 12 whole blood specimens analyzed per day by CVAAS. Urine samples were previously acidified with nitric acid to pH < 2. Total volume excreted was measured and recorded for each 24-h urine specimen. All whole blood samples were collected using the standard phlebotomy technique in Monoject trace element-free vacutainer tubes containing EDTA anticoagulant (Sherwood Medical Co., St. Louis, MO).

2.7. Calibration matrix

Urine was collected from a healthy individual for 24 h in an acid-leached plastic carbouy. The urine was acidified to a pH less than 2 with redistilled nitric acid. The acidified urine was mixed thoroughly and aliquoted into screw capped Sarstedt vials. This urine is the matrix used for the matrix calibration method described below.

2.8. Standardization and analysis

In the final analytical format used to produce quantitative mercury results, a set of calibrating standards containing 0–50 μg Hg/l in 2% HCl and 57 mg K$_2$Cr$_2$O$_7$/l were used to determine instrument response. These standards and a matrix urine were diluted 1:10 with a solution containing HCl and dichromate as above with 200 μg Bi/l as the internal standard. The ICPMS instrument was calibrated from high concentration to low using these matrix calibrators, as prescribed by Perkin-Elmer. Good Laboratory Practice (GLP) protocol would suggest that it should make no difference whether calibrators are analyzed in ascending or descending order. Reagent blanks contained deionized water in place of the urine matrix. Lowest actual mercury concentration introduced into the instrument was 0.05 μg Hg/l.
Urine samples were diluted 1:10 with the dichromate–HCl diluent and whole blood was diluted 1:20. Whole blood samples were vortexed to thoroughly mix diluent with the blood but not centrifuged. Minimal cellular debris and no protein denaturing was produced by 1% HCl.

2.9. Memory effect experiments

The effectiveness of dichromate, gold, and the ‘fast pump’ purge mode was determined by taking readings at 10-s intervals with a dwell time of 100 ms and 25 sweeps for the sampling sequences described as follows. To test equilibrium and washout, three blanks of the trial diluent were measured first. The sample probe was then inserted into the test solution containing matrix and mercury (or lead) plus the test diluent. The measurement sequence was started as the liquid sample entered the nebulizer. Measurements at 10-s intervals were accumulated until a steady state signal was observed (10–20 readings). The probe was then inserted back into the test diluent containing no matrix or mercury (or lead) and the measurements resumed. This sequence was followed rigidly for all test solutions so that differences in equilibrium and washout could be observed and calculated. For the trial of the ‘fast pump’ purge mode the ‘fast pump’ sequence lasted 20 s then the microprocessor reset the sample pump to the standard sampling speed of 1 ml/min.

Data was accumulated throughout the blank diluent, sample, washing sequence in this mode also.

2.10. CVAAS facility and method

The Perkin-Elmer (Perkin-Elmer Corp., Norwalk, CT) flow injection cold vapor mercury analysis system consists of the following components: Model 3100 spectrometer equipped with a 19-cm flow cell maintained at 100°C; FIAS 200 pump system with a 1-ml sample loop; AS 90 autosampler; EDL System 2 lamp power supply. The system is controlled with a Digital Equipment DECstation 325c computer and Perkin-Elmer controlling software. Results are printed on a Texas Instruments Omni 800/Model 855 printer. A complete description of this instrument and method is described elsewhere [9] but, the method will be described briefly here.

To every Pyrex 125 × 16-mm digestion tube, 0.2 g K₂S₂O₈, 4 ml of concentrated HNO₃, and 0.5 ml H₂SO₄ were added with thorough mixing. Blanks, controls, and blood samples were prepared by pipetting 0.5 ml of water, control, or sample into a digestion tube containing the oxidative mixture. Standards were prepared by pipetting 0.0, 0.05, 0.10, 0.20, 0.50, 1.0, and 2.5 ml of the 10 ng Hg/ml standard into separate digestion tubes containing the oxidative mixture. In addition, 0.5 ml whole blood was added to each standard tube as a matrix. For urine, a sample size of 1.0 ml was used. Standards, blanks, controls, bloods, and urines were placed in the dry block heater at 95°C for 30 min. Digestion was considered complete when foaming stopped and fumes containing oxides of nitrogen appeared above the digestion mixture. Allowing the digestion to proceed longer than 30 min was not detrimental to the final result. All blanks, standards, controls, and samples were diluted to 9 ml final volume with deionized water. Standard CVAAS analysis was performed on these samples using 5% stannous chloride prepared in 3% HCl.

ICP-MS mercury results were compared with CVAAS results for whole blood and urine samples.

3. Results and discussion

3.1. Mercury memory effects

The normal Elan 5000A sample pump-operating mode is a constant speed irrespective of the sample probe position. Typically the speed is set to deliver 1 ml/min to the nebulizer. In the ‘fast pump’ mode the pump is microprocessor controlled so that the pump speed is increased to 2.5 ml/min for 20 s each time the probe enters either a sample tube or the rinse solution. This ‘fast pump’ mode of sampling was first tested with urine matrix-based solutions containing 2% HCl with and without gold. We evaluated gold first because the effects of gold on memory have been much discussed at scientific meetings [15] and the
method has been the subject of literature from instrument manufacturers [15] and a USEPA environmental method [20]. Our results are displayed in Fig. 1, for ‘fast pump’ vs. normal sample delivery and for the addition of gold to a urine matrix containing 5 μg Hg/l. Gold was added at 1 μg/ml. Gold does enhance the overall mercury signal somewhat and the rise time of the mercury signal is shorter with gold irrespective of the pump speed. The presence of gold in the blank-rinse solution does increase the mercury blank signal but, the mercury enhancement is greater than the blank increase. In the washout part of the experiment it is clear that the presence of gold offers no advantage over HCl alone. The use of ‘fast pump’ to flood the spray chamber with blank-rinse solution is more effective at signal reduction than the presence of gold. The ‘fast pump’ mode reduces the washout time by half. In the normal sample delivery mode the signal returned to near blank levels at 140 s. With the ‘fast pump’ only 70 s was required. Use of nebulizer–spray chamber wash to reduce memory is not new. The development of a rapid clearing system using a combination of wash solution and high volume gas flush has been described [24]. Iron and zinc signals were reduced by 50000 × in approximately 20 s using this system [24]. While a ‘fast pump’ feature is standard on an ELAN 6000 ICP-MS, the system described here was designed for the ELAN 5000A by the Mayo Clinic Section of Engineering. The data in Fig. 1 is a composite of at least three experiments for each diluent combination.

In the next experiment HCl, HCl + Au, HCl + Cr₂O₇²⁻, and HCl + Au and C₂O₄²⁻ were evaluated in a urine matrix with mercury at 1.4 and 13.6 μg/l. ‘Fast pump’ sample delivery was used

![Mercury ICP-MS](image)

Fig. 1. Rise time, equilibrium, and washout for mercury ICP-MS signal with and without gold using normal sampling pump speed and ‘fast pump’.
Fig. 2. (A, B) Rise time, equilibrium, and washout for mercury in a urine matrix at 1.4 \( \mu g/L \) (A) and 13.6 \( \mu g/L \) (B) in (■) HCl, (+) HCl + Au; (○) HCl + dichromate, and (Δ) HCl + dichromate + Au using 'fast pump' only.
for all experiments. Fig. 2A,B show the raw signals with time for each diluent and blank–rinse combination. When dichromate is present, the mercury signal reaches steady state within 50 s of sample introduction whether gold is present or not. With HCl alone or with gold present the mercury signal continually increases. This is less evident in Fig. 2B with a higher mercury concentration. With HCl and gold, the washout takes at least 220 s. Even at 220 s some residual mercury signal can be seen in both figures. Memory and washout times are significantly less with dichromate present. When dichromate is present the signal drops to near baseline in 30 s or less at 1.4 µg Hg/l and approximately 60 s with 13.6 µg Hg/l. Memory effects are reduced whether gold is present with the dichromate or not. It appears that dichromate is the active agent for mercury memory reduction.

Dichromate was chosen for evaluation because it is routinely used to prevent titer change in mercury standard solutions [16]. It has been shown that acidification of solutions prevents loss of mercury by adsorption; however, acidification alone does not prevent loss by volatilization [16]. When dichromate alone was added to mercury solutions loss by volatilization was prevented but, loss by adsorption was not [16]. The combination of dichromate and acid prevented loss by both mechanisms [16]. It should be added that gold has been shown to be as effective as dichromate in solution loss prevention [16]. In our trials using aerosols however, dichromate is much more effective at controlling mercury memory effects than gold.

Dichromate was chosen for evaluation because it has been used in the oxidative digestion of biomedical samples prior to CVAAS [21]. The addition of dichromate to digestion solutions allowed the complete solubilization of insoluble

![Pb and Hg Comparison](image)

Fig. 3. Washout for mercury and lead with and without HCl-dichromate added to the argon aerosol gas. (■) 10 µg Hg/l. (+) 10 µg Pb/l.
mercury compounds such as cinnabar (HgS) [21]. Dichromate is also listed as a matrix modifier in the Zeeman graphite furnace atomic absorption spectrometric (ZGFAAS) determination of mercury [22]. With dichromate present a char temperature of 250°C was used without mercury loss [22]. In effect, dichromate prevents the reduction of mercury to the metal or mercury precipitates such as sulfides and calomel. We assume that dichromate prevents reductive volatilization and does not allow appreciable mercury vapor or insoluble compounds to form when mercury solutions are sprayed into a spray chamber.

In our last experiment Hg and Pb memory were compared after introduction of 10 μg/l of each analyte. Fig. 3 shows the data with the baseline expanded so that the washout data is more visible. In this experiment, a urine matrix containing 10 μg Hg and Pb/l was aspirated after which the liquid flow was stopped. Only argon carrier gas was flowing through the sample introduction system. Data was collected for 100 s before the flow of blank-rinse solution was resumed. It can be seen that the lead signal dropped to near blank level within 20 s after the liquid flow was stopped. Mercury signal did drop when the liquid flow was stopped, but not to the blank level. Some residual signal remained until the HCl–dichromate liquid flow was resumed. Within 10 s after the liquid flow was resumed, the mercury signal dropped significantly. Within 50 s the signal dropped to the lead signal level. With resumption of liquid flow, the lead signal was essentially unchanged. While this experiment does not tell us whether mercury is bound to the spray chamber surface or whether mercury simply resides in the dead volume, it does show that dichromate is effective at removing the residual mercury and reducing memory.

In summary, no data for nitric acid is presented because of poor recovery [19]. We also observed extensive memory effects when 1% nitric acid was used in the diluent. Gold has been used effectively in mercury solution preservation [16] but, in spray chamber memory reduction, gold is not as effective as dichromate. Washout times do vary with mercury concentration. At 13.6 μg Hg/l washout was 60 s. At 1.4 μg Hg/l washout was 30 s or less. Others have reported washout times of 45 s [14], 130 s [18], and 180 s [19]. For quantitative analysis 90 s between samples seems appropriate.

### 3.2. Mercury quantitation

#### 3.2.1. Detection limits

Detection limits were determined on 4 separate days in routine analytical runs. The standard used contained 5 μg Hg/l in a urine matrix. The detection limit is defined as the mercury concentration calculated to produce a signal three times the standard deviation of the blank readings. In this experiment 12 blank readings were used to calculate the standard deviation of the background. The average detection limit was 0.15 μg Hg/l in the original sample before dilution. Our average detection limit is comparable to other ICPMS methods using solution nebulization.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Day-to-day results for the analysis of QC samples by ICPMS and CVAAS</th>
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<tbody>
<tr>
<td>Control</td>
<td>Certified value&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>NIST 2670 Normal</td>
<td>(2)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>NIST 2670 Elevated</td>
<td>105 ± 8</td>
</tr>
<tr>
<td>Bio-Rad Lot 44502</td>
<td>74.1 (range: ±14.8)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Bio-Rad Lot 60902</td>
<td>72.5 (range: ±14.8)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Blood-inorganic spike</td>
<td>20 Nominal added</td>
</tr>
<tr>
<td>Blood-methyl mercury</td>
<td>20 Nominal added</td>
</tr>
</tbody>
</table>

<sup>a</sup>All values are microgram per liter; all other ± values are 1 S.D.
<sup>b</sup>Information value only.
<sup>c</sup>Acceptable range listed, not S.D.
Fig. 4. (A, B) Comparison of ICP-MS results for whole blood (A) and urine (B) with target concentrations for Quebec interlaboratory comparison samples.
3.2.2. Quality control

Day-to-day results for several urine and whole blood controls are shown in Table 2. Results for both ICPMS and CVAAS methods compare favorably with certificate values for urines. Inorganic and methyl mercury blood controls were prepared in house. Whole rabbit blood was supplemented with inorganic mercury and methyl mercury chloride at 20 \( \mu g/l \). The whole blood controls were digested with nitric acid–sulfuric acid–persulfate before CVAAS analysis [9]. For ICPMS analyses whole blood controls were diluted 1:20 with the HCl–dichromate diluent and vortexed to thoroughly mix the blood with diluent. The diluted controls were aspirated directly into the nebulizer without further manipulation. No CVAAS results are shown for the more recent Bio-Rad urine control. The CVAAS method was no longer in use when this Bio-Rad lot was evaluated. NIST 2670 Normal Level was analyzed by the ICPMS only.

3.2.3. Interlaboratory comparisons

Urine and whole blood interlaboratory comparison samples from the Centre de Toxicologie du Quebec were analyzed by ICP-MS and CVAAS. The results for ICP-MS are shown in Fig. 4A for whole bloods and Fig. 4B for urines. High and low acceptable analysis limits are also drawn in the figures. ICP-MS gives results that correlate well with the certified concentrations. In general, blood results are close to the identity line but urine results are somewhat low. In all cases few results are outside the acceptable limits.

3.2.4. Patient samples

Our evaluation of the ICP-MS method included the analysis of routine whole blood and urine samples by ICP-MS and CVAAS. For urine, 456 samples with concentrations from \(< 1 \mu g/specimen\) to 25 \( \mu g/specimen\) were analyzed by both techniques. The resulting regression equation is: \( y = 0.93x + 1.0\) with a correlation coefficient of 0.8763. For whole blood, 241 samples with concentrations up to 35 \( \mu g/l\) were

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**Fig. 5.** Comparison of ICP-MS with CVAAS results for urine samples positive for mercury.
analyzed and the equation is: \( y = 1.1x + 0.2 \) with a correlation of 0.9357.

A group of 30 urines found to be in the normal range by CVAAS were sequestered and analyzed in duplicate by CVAAS and ICP-MS in a 2-week period. The average deviation in duplicates by CVAAS was 1.2 \( \mu \)g/l. The largest difference in results was 4 \( \mu \)g/l. Results ranged from < 1 \( \mu \)g/l to 10 \( \mu \)g/l. The average deviation for ICP-MS duplicates was 0.7 \( \mu \)g/l with the largest difference of 3 \( \mu \)g/l. Results for the same samples ranged from < 1 \( \mu \)g/l to 14 \( \mu \)g/l. Correlation of ICP-MS with CVAAS was \( y = 1.01x + 0.3 \) with a correlation coefficient of 0.8316.

In a final experiment a group of urines positive for mercury by CVAAS were analyzed by ICP-MS. The results are shown in Fig. 5. The figure shows that ICP-MS compares very well with CVAAS.

4. Conclusion

We conclude that dichromate plus hydrochloric acid as a diluent and in the wash solution is effective at minimizing mercury memory. We further conclude that the ‘fast pump’ mode used in the wash cycle facilitates mercury washout. The ‘fast pump’ mode used at the beginning of a sample reading cycle facilitates mercury signal equilibrium. The use of dichromate is compatible with heavy metal screening for Cd, Pb, Tl, and As. Mercury can be incorporated into the screening method for these other metals.

References