



Potential application of a semi-quantitative method for mercury determination in soils, sediments and gold mining residues

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Semi-quantitative low-cost method for mercury determination in soil, sediments and mining residues.

Abstract

An alternative, low cost method for analyzing mercury in soil, sediment and gold mining residues was developed, optimized and applied to 30 real samples. It is semiquantitative, performed using an acid extraction pretreatment step, followed by mercury reduction and collection in a detecting paper containing cuprous iodide. A complex is formed with characteristic color whose intensity is proportional to mercury concentration in the original sample. The results are reported as range of concentration and the minimum detectable is 100 ng/g. Method quality assurance was performed by comparing results obtained using the alternative method and the Cold Vapor Atomic Absorption Spectrometry techniques. The average results from duplicate analysis by CVAAS were 100% coincident with alternative method results. The method is applicable for screening tests and can be used in regions where a preliminary diagnosis is necessary, at programs of environmental surveillance or by scientists interested in investigating mercury geochemistry.

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1. Introduction

The growing interest in non-sophisticated semi-quantitative methods has been recognized by the increasing number of scientific publications and offered commercially available tests, mainly for clinical analysis (screening tests for glucose and urea in blood), production control (cooling water used in industry, air quality in working areas), and environmental protection (lake and stream limnology studies, water quality analysis systems) (Jungreis, 1985; Weiz and Lepper, 1985). Simplicity, low-cost, quickness, on-site determinations, and the possibility of processing by unskilled personnel are the main advantages of these techniques, replacing more complicate and time-

consuming quantitative methods. Most of the methods are based on colorimetry, titration with/on impregnated paper, area or length, and temperature or volume (Jungreis, 1985; Weiz and Lepper, 1985). Some test methods were proposed for determining metals in solutions: indicator powder or sorbent as glass indicator tubes (Cd, Co, Cu, Fe, Pb, Morosanova et al., 1997); polyurethane foam loaded with selective reagents as glass column (Cd, Cu, Hamza et al., 1985); ion exchange chromogenic polydentate irregular α -cellulose as strips or discs (Ag, Cd, Co, Cu, Fe, Hg, Pd, and Zn, Ostrovskaia, 1998), and irregular cellulose bearing fragments as indicator paper (Cd, Co, Cu, Fe, Hg, Ni, and Zn, Ostrovskaia et al., 2004).

Yallouz et al. (2000) firstly idealized mercury semi-quantitative method (SQM) for fish analysis. It is colorimetric, low cost, easy to operate, and attends to the WHO recommendations for fish consumption (WHO, 1990). It was developed to monitor areas affected by mercury pollution. Most of these

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places are isolated from urban centers, with lack of laboratory infrastructure, which precludes the access to conventional mercury analysis, as for example, the Cold Vapor Atomic Absorption Spectrometry (CVAAS) (Yallouz et al., 2000).

SQM fish determination is performed in two steps: an acid digestion, using an acid digestion solution of $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{V}_2\text{O}_5$ (sulfonitric solution), followed by a visual determination using a detecting paper covered with an emulsion that develops a characteristic color due to the $(\text{HgI}_4)^-$ complex formation (Yallouz et al., 2000).

Since its development, SQM fish determination quality assurance control has been made through comparison with a quantitative method, and in January 2002, complementary action was implemented: participation in interlaboratory program of the Mercury Quality Assurance Program, coordinated by the Canadian Food Inspection Agency.

The easy operation of the SQM made possible its diffusion through training of local users in Rio de Janeiro and Itaituba (Brazil), and Manado (Indonesia). New users from Sudan, Laos, Zimbabwe, and Indonesia were trained at Center for Mineral Technology (CETEM) in July 2004 and in the next future SQM will be implemented at those countries.

The objective of this paper is to detail the development, optimization and evaluation of the application potential of the SQM for mercury determination in soils, fluvial sediments and gold mining residues. The possible applications of the method in multi-disciplinary geosciences and environmental researches groups will also be discussed.

2. Materials and methods

2.1. Samples

The samples of soil, fluvial sediments and gold mining residues were collected at two small-scale gold mining areas in the Brazilian Amazon, São Chico ($06^\circ 25' 31'' \text{ S}$, $56^\circ 02' 99'' \text{ W}$) and Creporizinho ($06^\circ 50' 14'' \text{ S}$, $56^\circ 35' 00'' \text{ W}$), Pará State, in a field campaign at July 2003.

The total of 30 samples were air-dried and homogenized in porcelain mortar. After that they were wet sieved in order to separate into two grain size fractions: less than $74 \mu\text{m}$ ($-200 \#$ mesh) and greater than $74 \mu\text{m}$ ($+200 \#$ mesh). Each fraction has been dried at 40°C , and kept in polyethylene bottles.

For the development step, 22 samples (four soils, 13 fluvial sediments and five gold mining residues) were analyzed. In order to evaluate the applicability of the method for different chemical compositions, the selection criterion was based on the difference in coloring, which apparently suggests distinct geochemical and mineralogical compositions.

For the optimization step, three samples (two fluvial sediments and one gold mining residue) were divided into sub-samples and analyzed separately. The following parameters were tested: elimination of the filter phase, decrease of the extraction time and decrease of the SnCl_2 original volume.

For the applicability study of geochemical affinity between particle size and mercury concentration, nine samples (four fluvial sediments, five soils, and one gold mining residue) in different grain sizes and/or in bulk sample were analyzed.

2.2. Methods

All chemicals used were of analytical reagent grade. Sample digestion was accomplished by Aqua Regia and 5 mg of dimeticona solution (anti-foam), and solution reduction was completed by the addition of 50% w/v of tin chloride in hydrochloric acid 50% w/v. The Aqua Regia is prepared using three parts of HCl and one part of HNO_3 , some minutes before starting analysis.

Hot plates with sand baths were used for samples pretreatment, and aquarium pumps as mercury vapor carrier.

The methodology to prepare and store detecting paper follows Yallouz et al. (2000). The intensity of the color developed by the samples is visually compared with color scale derived from well known Hg^{2+} solutions that are simultaneously analyzed. The series of standard Hg^{2+} solutions was prepared by water dilution of a 1000 ng/g stock solution $\text{Hg}(\text{NO}_3)_2$ certified reference materials (Merck, Germany). The standard solutions are chosen according to the expected analytical results. To optimize range color discrimination, a standard illumination (incandescent lampshade) must be used.

Yallouz et al. (2000) recommends the use of at least three different concentration ranges for calibration curve. The SQM lower determination limit of total mercury is estimated visually to be 100 ng/sample grams (Yallouz et al., 2002). Results are considered satisfactory when quantitative arithmetic average values fall in the SQM concentration ranges.

For quantitative comparison studies an Automatic Mercury Analyzer Hg-3500 Spectrometer (KK. Sanso SS), using a Vapor Generation Accessory (VGA), was used. The Environmental Mercury Speciation Laboratory (Laboratório de Especificação de Mercúrio Ambiental – LEMA) of the Mineral Analysis Coordination (Coordenação de Análises Mineraiis – COAM), CETEM performed the analyses. The method used follows the methodology developed by Akagi and Nishimura (1991), which involves sample digestion. Two milliliters of an oxidant 1:1 acid mixture ($\text{HClO}_4:\text{HNO}_3$) are added drop wise into 0.5 g of sample, previously weighted in a 50 mL volumetric flask. Then, 1 mL of water is added. The mixture is carefully heated to $230\text{--}250^\circ \text{C}$ during 20 min. After cooling, the solution is diluted up to 50 mL, and samples were analyzed at least twice to guarantee result quality. For quality assurance/quality control sets (QA/QC) a standard reference material of the National Institute of Standards and Technology (NIST1633b, coal fly ash) was determined for each set of 10 unknown samples. All results obtained from reference material analysis fall into expected interval.

3. Results

3.1. Development step

For soils, sediments and gold mining residues pretreatment, an acid mixture composed of 3:1 $\text{HCl}:\text{HNO}_3$ (Aqua Regia), were used instead of fish acid digestion solution. The last one interferes colored complex development by elementary iodine liberation.

Therefore, the experiments were made using the following procedure: 10 g of sample are heated for two hours on a hot plate at 80°C in a digestion flask (Erlenmeyer stoppered with a water filled cold finger, Fig. 1), with 25 mL of Aqua Regia and two drops of anti-foaming.

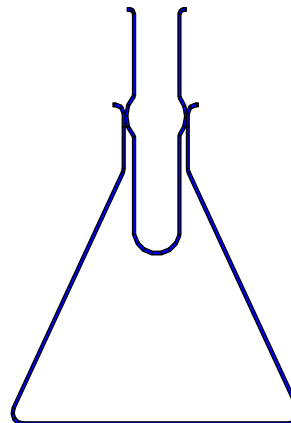


Fig. 1. Extraction System – Erlenmeyer with cold finger.

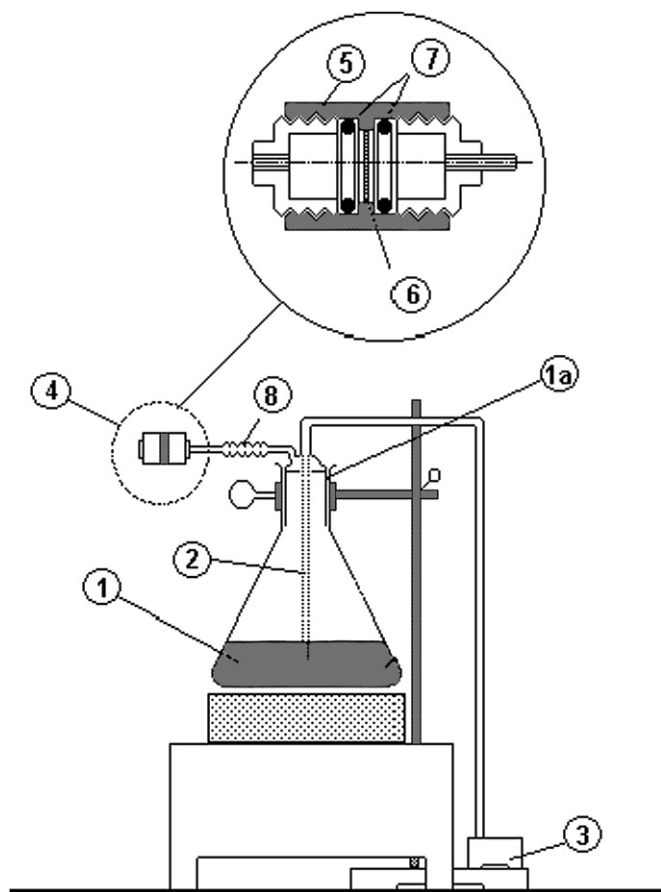


Fig. 2. Semi-quantitative Determination System (1 – analytical solution; 2 – aeration duct; 3 – aquarium pump; 4 – detection system; 5 – PVC paper support; 6 – detecting paper position; 7 – o-rings; 8 – mini-condenser).

After cooling, 50 mL of deionised water are added and the mixture is filtered. The analytical solution is transferred to a determination flask (Fig. 2), and 10 mL of the reducing agent solution (50% w/v of tin chloride in hydrochloric acid 50% w/v) are added. Then the aeration system (aquarium pump) is turned on. Vapor mercury is forced to pass through a detecting paper (in a PVC filter holder device, Fig. 2), containing cuprous iodide, forming reddish colored complex (Fig. 3). The samples were analyzed at least twice to guarantee the result quality. Simultaneously, standard solutions are prepared with concentrations similar to the expected ones defined preliminarily. The determination of mercury concentration range is obtained

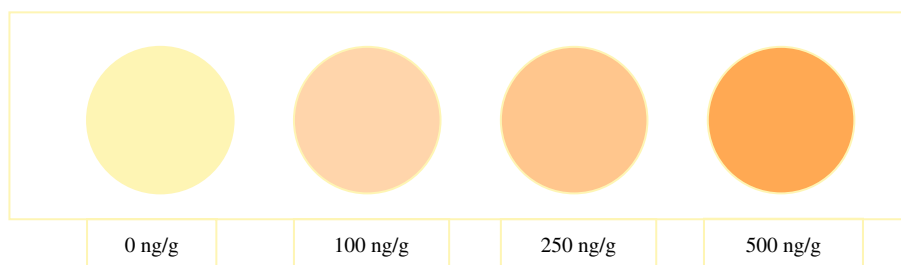


Fig. 3. Detecting paper, containing cuprous iodide, forming a reference materials concentration range scale of reddish color.

Table 1

Comparison of results obtained by quantitative (QM) and semi-quantitative (SQM) methods of mercury concentration in environmental samples

Mining site	Sample	SQM (ng/g)	QM (ng/g)
São Chico	SD-01 ^a	300–600	544
	SD-02 ^a	>2000	2700
	SD-03 ^c	>2000*	1930
	SD-04 ^c	>2000	2490
	SD-05 ^a	>2000	2390
	SD-06 ^a	<200	98.6
	SD-07 ^a	<200	127
	SD-08 ^c	200*	210
Crepo-rizinho	SD-09 ^c	<200	159
	SD-10 ^a	<200	95
	SD-11 ^a	<200*	258
	SD-12 ^b	200*–400	308
	SD-13 ^c	200*–400	226
	SL-01 ^c	200–400*	387
	SL-02 ^c	600*–1000	613
	SL-03 ^c	>2000	2370
	SL-04 ^c	200*–400	279
	MRS-01 ^a	>2000	4430
	MRS-02 ^c	>2000	2150
	MRS-03 ^b	600–1 200*	1080
	MRS-04 ^c	100–200*	239
MRS-05 ^c	200–400*	330	

SD = sediments; SL = soils and MRS = gold mining residues; * = closer to; samples fractions: a = *natura*, b = >200# and c = <200#.

by visually comparing the paper color developed by the samples with that of the simultaneously analyzed standard solutions (Fig. 3).

The results obtained by quantitative (QM) and semi-quantitative (SQM) methods were compared and the results are in Table 1. Some of them presented colors close to one of concentration range limits and the others in the middle of the class interval, but their concentration ranges were 100% coincident with the average results from duplicate analysis by CVAAS.

3.2. Optimization step

To warrant the quality, the experimental results of some samples were compared not only to quantitative analysis, but also to the SQM analysis, using its original procedures (Table 2). The results at Table 2 demonstrate that SQM efficiency was not affected by filtering stage elimination, SnCl₂ volume decreasing to 5 mL, and time extraction decreasing to 30 min.

Table 2
Results of optimization step, samples collected at São Chico and Creporizinho mining sites

Sample/ sub-sample	Filter	SnCl ₂ volume (mL)	Extraction time (min)	Results semi- quantitative (ng/g)	Results quantitative (ng/g)
SD-05 ^a					2390
1	Yes			>2000	
2	No			>2000	
3	No			>2000	
4	No			>2000	
SDB ^b					697.3
1			120	600–1000	
2			90	*600	
3			90	600–1000	
4			60	*600	
5			60	*600	
6			60	600–1000	
7			90	600–1000	
●SD14 ^a					95
1	Yes	5	30	>100	
2	Yes	5	30	*100	
SD15 ^c					210
1	Yes	5	30	<300	
2	Yes	5	30	<300	
3	Yes	5	30	<300	
SD16 ^c					127
1	Yes	5	30	100–300	
2	Yes	5	30	100–300	
3	Yes	5	30	100–300	
●SD17 ^c					308
1	Yes	5	30	>300	
2	Yes	5	30	>300	
3	Yes	5	30	>300	
MRS-03 ^b					1 080
1		10	120	>1000	
2		5	30	>1000	
3		5		>1000	
			30	*1000	
4		5	30	>1000	
MRS06 ^c					1010
1	Yes	5	30	*1200	
2	Yes	5	30	<1200	
3	Yes	5	30	*1200	
●MRS07 ^a					258
1	Yes	5	30	*300	
2	Yes	5	30	*300	

SD and SDB = fluvial sediment; MRS = gold mining residue; 1–7 = sub-samples; * = closer to; samples fractions: a = natura, b = 200# and c = <200#; ●Creporizinho mining site.

In consequence, both analysis time and laboratorial resources expend decrease.

3.3. Application study

For all samples analyzed, it was observed an increase of the mercury concentration in smaller grain sizes (Table 3), probably associated to the higher specific surface of the fine grains and metal, related directly to the texture of soil or sediment.

Table 3
Mercury concentration at different particle sizes (sampling mining sites: sediments – São Chico, soils and residue – Creporizinho)

Sample	Sample fractions				
	<200#	100#	80 #	>48 #	Natura
SD-03	>2000*		1200–2000*	100–300	
SD-04	>2000		<100		600–1200*
SD-08	100–200			<100	100*–300
SD-12	200*–400			<100	<100*
SL-01	200–400*			100–200	100–300
SL-02	600*–1000			100–200	100–300*
SL-03	>2000			100–200	300–600*
SL-05	1200–2000*			<100	100–300
MRS-01	>2000	600–1200	600*–1200		

* = closer to.

4. Discussion

Since the 70's mercury environmental contamination and its consequences to human health had been studied (Lacerda and Solomons, 1998). In Brazil, besides its use in industrial activities, mercury is also used in artisanal and small-scale gold mining generating poisonous residues during the amalgam process to miners and environment (gravity concentration, burning in open pans, and melting in gold shops) (Malm et al., 1995).

Mercury liberated in these processes can be deposited on surrounding soils and sediments, considered as mercury reservoirs. Mercury is concentrated in the smaller grain sizes, where the specific surface area is higher. Certainly, among the physical-chemical properties (like clay mineralogy, organic matter, etc.), that could affect mercury adsorption in soil or sediment samples (Rodrigues-Filho and Maddock, 1997; Wasserman et al., 2001), texture plays an important role. Therefore, as many variables can influence mercury retention in different geoenvironments, geochemical modeling of this metal becomes very complex.

Some semi quantitative and/or qualitative methods are used in geochemical explorations, mainly in preliminary prospecting work, even been applied in the field (Jungreis, 1985). Jungreis (1985) describes a semi quantitative field test for mercury determination in soil rocks: the mercury iodide volatilization method, most effective in rocks containing cinnabar, which use dithizone as reagent.

Our mercury colorimetric method was developed to analyzed soils, fluvial sediments and gold mining residues, and the results in concentration ranges obtained are comparable to quantitative ones (Table 1). It couldn't be applied in the field, because it is necessary a small laboratory infrastructure and a trained person (Yallouz et al., 2002).

Obtained results at optimization step (Table 2), demonstrate that SQM could be more simples without losing efficiency, and that parameters optimizations allows benefits like: decreasing analysis time and effluent environmental risk, and expenses with laboratory glassware, filter paper, electric energy and chemical reagents.

The results of potential application study (Table 3) denote that it is possible, using SQM, to identify a geochemical

affinity between particle size and mercury concentration. This study demonstrated SQM potential application in geosciences, agrarian and environmental researches where a semi-quantitative diagnosis of mercury concentrations is enough.

5. Conclusions

As the described SQM method is simple and with low-cost, it could be recommended as an alternative method for screening programs of environmental surveillance. To be used all that is necessary is a small laboratory infrastructure and a trained person (Yallouz et al., 2002). Besides soils, sediments and gold mining residues described in this paper, it is also possible to analyze fish and urine, thus amplifying the possibilities of continuous environmental and human health monitoring diagnosis in areas with historical of mercury pollution.

The potential application potential of SQM to geosciences research groups, agrarian sciences and environmental sciences (e.g. pedogeochemical, sedimentological, oceanographical, agronomical and geographical researches) is conspicuous in studies where a semi-quantitative diagnosis is enough. As in general, mercurial quantitative analyses are very expensive, SQM can become a very interesting tool for scientists of those areas.

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