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Short Communication

Cationic Interference in Mercury Analysis by Cold Vapour Atomic Absorption Spectroscopy

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Abstract. The cationic interference in the analysis of mercury at trace level by cold vapour atomic absorption spectroscopy (CVAAS) has been investigated. Different cations (Na^+, K^+, Fe^{2+}, Zn^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}) of varying concentrations are examined as possible interferents in the analysis of mercury. Na^+, Fe^{2+}, Zn^{2+} and K^+ did not show any affect due to their presence in the detection of mercury while Co^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+} had a marked influence on mercury recovery and can be suggested as possible interfering agents for this method of Hg analysis.

Keywords: mercury analysis, cold vapour technique, cationic interference

Mercury is a proven toxic element, even at trace levels and can cause serious human health disorders (Kagaya *et al*. 2004; Hatje *et al*., 1998; Bidone *et al*., 1997a; 1997b). Interference in an analysis is as important as the analysis itself. Several analytical techniques exist to determine mercury at trace levels, among which cold vapour atomic absorption spectroscopy is widely used (Silva *et al*., 2005; Bermejo-Barrera *et al*., 1996; Katiuska *et al*., 1996).

A method has been devised for the indirect determination of iodide based on its interference with the determination of mercury (Afkhami and Khalafi, 2005; Haase and Broekaert, 2002; Sun and Julshamn, 1987; Kuldvere, 1982).

Presence of sulphate ions do not interfere in the analysis (Kolthoff and Sandell, 1952). Copper interference has been reported by Csuros and Csuros (2002), while cobalt interference has been reported by Paklepa *et al*. (2001). Similarly, under ambient conditions, silver, gold, copper, zinc, and aluminum readily form amalgams with liquid or gaseous elemental mercury (Ebadian, 2001; Andren and Nriagu, 1979).

This study is confined to cationic interference confronting in the analysis of mercury by cold vapour atomic absorption spectroscopy (CVAAS). All measurements were recorded on a double beam atomic absorption spectrophotometer (Perkin-Elmer Analyst 700) equipped with cold vapour atomizer (Perkin Elmer MHS-15 mercury hydride system). All the chemicals used were 'AR' grade. A 1000 ppm mercury standard solution of AAS reagent was used (i.e. 4.98 mmol / L Mercuric nitrate in 5 M HNO_3). Other chemicals used were HCl (11.5 M.), $KMnO_4$, H_2SO_4 (98%), HNO_3 (65%) and NaOH.

Mercury stock solution (1000 ppm) was diluted to 1.0 ppm with deionized water, when required. Stock solutions of 1000 ppm strength of different metal ions such as Na, K, Fe, Zn, Cr, Co, Ni, Cu were prepared from NaCl, KCl, $(NH_4)_2SO_4.FeSO_4.6H_2O$, $Zn_3(PO_4)_2.4H_2O$, $CrCl_3.6H_2O$, $CoSO_4.7H_2O$, $NiSO_4.6H_2O$, and $CuSO_4.5H_2O$ salts, respectively. In order to avoid hydrolysis in metal stock solutions, 5 mL of concentrated 37% HCl solution was added.

Dilutions of 200 ppm, 400 ppm, 600 ppm and 800 ppm were prepared in 100 mL volumetric flasks from the 1000 ppm stock solution, with the addition of one drop of 5% $KMnO_4$ solution and 1 mL of 1.0 ppm standard Hg solution using a micropipette, to give a final solution of 10 ppb Hg concentration. Potassium permanganate was added to reduce possible interference due to sulphide ions (Csuros and Csuros, 2002). Standard solution 10 ppb Hg was also prepared in a similar way without addition of any metal ion. The solutions were analyzed with AAS using MHS 15 system. The lamp current was set at 6 mA, with an integration time of 25 sec. The linear calibration mode was selected, while peak area was used for all calculations. The slit bandwidth was kept at 0.7 nm, at low slit height. Argon gas was purged at 3.0 bar pressure and plunger was held for 5-10 sec in each run.

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All over 10 mL aliquot of 10 ppb Hg (II) calibration standard was used. A 3% $NaBH_4$ was prepared in 1% NaOH solution. One drop of 5% $KMnO_4$ solution was added as stabilizing agent in each analysis run. 10 mL of acid mixture (prepared by adding 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 and 92.5 mL of distilled water) was also added prior to the reduction step.

All the metal ions were scanned up to 1000 ppm with 10 ppb of added Hg (II) and the results are presented in Table 1 and Figs. 1-2.

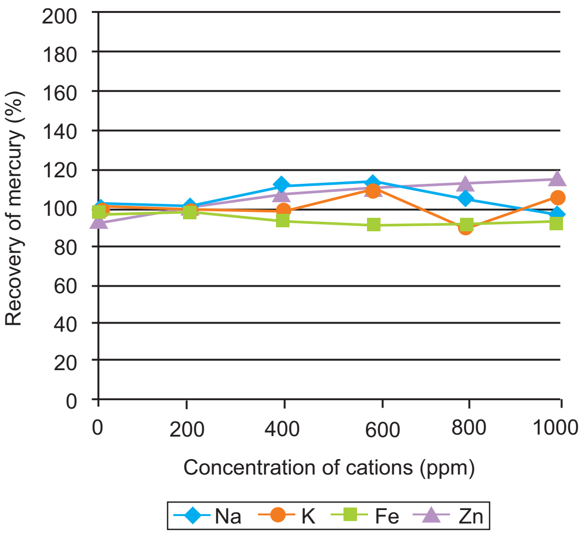

Fig. 1. Profile for cations that do not affect mercury recovery.

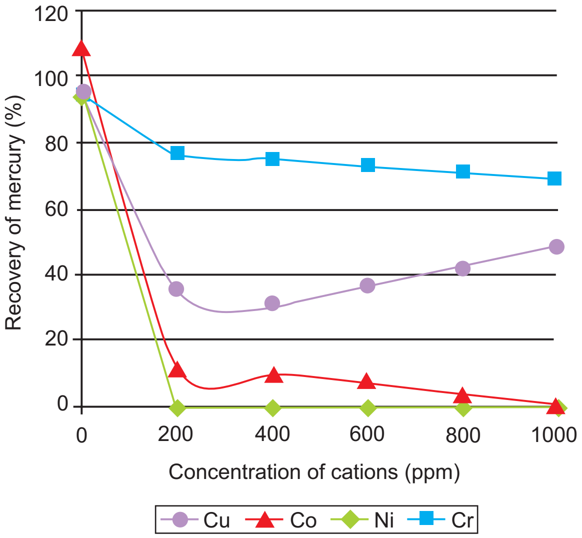

Fig. 2. Interfering affect of cations on recovery of mercury.

Table 1. Recoveries of 10 ppb Hg(II) at different concentrations of cations

Cationic conc.(ppm)	% Recovery of Hg(II) in presence of Na	K	Fe	Zn	Cr	Co	Ni	Cu
0	101.0	95.3	99.0	93.0	95.0	109.0	94.8	96.0
200	100.5	98.0	97.0	100.0	77.0	12.0	ND	36.0
400	111.0	98.3	93.0	107.0	75.0	10.0	ND	31.0
600	112.0	109.2	90.0	109.5	73.0	7.7	ND	37.0
800	104.0	89.8	91.0	112.0	71.0	4.0	ND	43.0
1000	96.0	105.1	92.0	114.0	68.8	0.8	ND	49.0

ND: not detected

Among the investigated cations, Na^+, K^+, Fe^{2+}, and Zn^{2+}, did not show any interference in mercury analysis by cold vapour atomic absorption spectroscopy, while Cr^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+} significantly reduced the mercury signal, forming characteristic patterns. The Pearson correlation coefficients corroborate that Co (II) and Cr (III), are preferentially reduced prior to the Hg (II) ions because of being present in a greater concentration (Johnson and Kuby, 2008). However, the interference due to presence of Ni (II) and Cu (II) could be due to amalgamation or competitive inhibition or both. The obtained information can help to identify the presence of possible interferents in the sample matrix. This study does not recommend the use of cold vapour technique for mercury analysis if the samples contain more than trace amounts of Cr^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions.

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