



Sono-induced cold vapour generation interfaced with capacitively coupled plasma microtorch optical emission spectrometry– analytical characterization and comparison with atomic fluorescence spectrometry

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ARTICLE

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Sono-induced cold vapour generation in 0.2 mol L⁻¹ formic acid has been interfaced for the first time with a low power (10 W) and low argon consumption (100 mL min⁻¹) capacitively coupled plasma microtorch for mercury determination by optical emission using a low resolution microspectrometer. The method meets the requirements of green analytical chemistry in terms of the derivatisation method, cost-effective conditions for plasma generation and miniaturized instrumentation. The method is based on sample ultrasonication in a batch reactor, purging of mercury vapour, moisture removal from vapour in a Nafion tubing, Hg preconcentration on a gold filament microcollector, thermal desorption and introduction of mercury vapour into plasma *via* an Ar stream. Emission episode spectra of Hg were recorded at 253.652 nm. Under the optimized conditions it was found a detection limit of 5.0±0.3 ng L⁻¹, better than 12 ng L⁻¹ obtained by atomic fluorescence spectrometry after chemical cold vapour generation with SnCl₂. The analytical capability of the new method was demonstrated by analysing certified reference materials and real samples of fish tissue, soil and sediment mineralized in acid mixture. The method is highly sensitive and the matrix effects associated to cold vapour generation were avoided by sample dilution. Mercury was determined using the external calibration with recovery and precision in the range of 96.3–104.5% and 0.8–7% respectively. No systematic error against atomic fluorescence with chemical cold vapour generation using SnCl₂ was observed.

1. Introduction

Miniaturization of instrumentation and development of friendly analytical methods meeting requirements in terms of both figures of merit for particular applications (detection limit, precision/accuracy) and green chemistry (low reagent/sample consumption, fast sample treatment, harmless solvents and derivatising agents, diminished laboratory wastes, use of clean energy like ultrasonic and microwave) are flourishing.¹

One of the research directions in the field of green analytical chemistry related to elemental analysis requiring a derivatisation step is the use of UV photo-induced or sono-induced cold vapour generation (SICV) as alternatives to the conventional chemical conversion with SnCl₂- or NaBH₄-HCl systems.²⁻¹² Ultraviolet or ultrasound irradiation as means to create volatile analyte species are based on the rise of reducible species (hydrogen, carbonyl, ketene, etc) in the presence of a low molecular weight organic acid (usually formic or acetic

acid) serving as reaction medium and derivatising agent.^{3,12,13} These non-conventional approaches provide major advantages over classical techniques using chemical derivatisation such as lower cost by eliminating expensive chemical reagents, use of non-hazardous organic acids, diminished interferences and easier optimization of analytical systems by decreasing the number of variables influencing CV generation. Recent achievements in chemical CV and hydride generation in atomic and mass spectrometry were reviewed.¹⁴⁻¹⁷ Microplasmas generated in simple construction torches running at low power and low Ar/He consumption, easy to be embedded in miniature analytical systems, equipped with low resolution microspectrometers, represent another advance in green analytical chemistry.¹⁸⁻²⁰ The analytical capability of various microplasma sources was demonstrated for simultaneous multielemental analysis of liquid microsamples, simultaneous determination of As and Sb after hydride generation or Hg quantification following CV generation.²¹⁻³⁵ Until now it has

not been investigated the opportunity of coupling the sono- or UV promoted CV generation with a microplasma/microtorch for mercury determination. Thus, the aim of the present work was to investigate for the first time the capability and usefulness of the sono-induced cold vapour generation combined with capacitively coupled plasma microtorch optical emission spectrometry (SICV- μ CCP-OES) for Hg determination. The method is based on Hg CV evolution in formic acid medium occurring in a batch sonoreactor, on-line Hg vapour preconcentration on a gold filament microcollector, entering of Hg vapour into the low-power and low Ar consumption plasma and record of successive emission episodes using a low-resolution microspectrometer. The novel SICV- μ CCP-OES analytical system was characterized in terms of optimal instrumental parameters and experimental conditions as well as interference from concomitant ions influencing CV generation and figures of merit. Limit of detection and quantification, precision and accuracy were established and compared with those found in the conventional cold vapour generation atomic fluorescence spectrometry (CV-AFS) using the SnCl₂-HCl system as reducing agent. The limit of detection was also compared with that achieved in other microplasma sources used in atomic emission spectrometry. The usefulness of the SICV- μ CCP-OES method as alternative to CV-AFS was demonstrated by Hg quantification in biological and environmental CRMs, and test samples. The protocol included the external calibration, sample digestion in acid mix and an appropriate dilution of the digest so that concomitant concentration to be low enough to avoid interference on CV generation in solution.

2. Experimental

2.1. Reagents, standard solutions and CRMs

Formic acid 98–100% (w/w) suprapure for trace analysis, nitric acid ultrapure 60% (w/w), hydrochloric acid 30% (w/w) ultrapure, hydrofluoric acid 40% (w/w) suprapure, boric acid suprapure, hydrogen peroxide 30% (w/w) pro analysis, KBr suprapure, KBrO₃ pro analysis, stock solution of 1000 μ g mL⁻¹ Hg and ICP multielement standard solution IV of 1000 μ g mL⁻¹ Merck (Darmstadt, Germany) were used. Solutions of formic acid with concentration in the range 0–1 mol L⁻¹ and stock solution of 10 ng mL⁻¹ Hg were used to optimize the experimental variables. Before use, the solutions of formic acid were subjected to supplemental ultrasonic purification for 2x5 min so that the residual Hg concentration fell below the quantification limit in SICV- μ CCP-OES. The sono-reactor vessel, PTFE digestion vessels and glassware were cleaned with 10% (v/v) BrCl solution resulted by dissolving KBr and KBrO₃ in concentrated HCl as described earlier.³¹ Certified reference materials of soil (RTC-CRM048-50G Trace Metals Sand 1, RTC-CRM025050 Soil Sandy Loam-Metals, LGC 6141 Soil contaminated with clinker ash, LGC 6135 Soil-Hackney Brick Works), sediments (BCR 240R Lake Sediment, NCSDC 78301 River Sediment), fish tissue and hepatopancreas

tissue (DOLT-4 Dogfish liver, BCR 463 Tuna Fish, TORT-2 Lobster Hepatopancreas) purchased from LGC Standards (Wesel, Germany) were analysed to check the accuracy of measurements. Milli-Q water (18.2 M Ω cm⁻¹ resistivity) was prepared in laboratory in a Milli-Q system Millipore (Bedford, USA).

2.2. Sample preparation

Amounts of 500 mg CRMs or test samples of fish or organ tissues were digested with 9 mL HNO₃ and 3 mL H₂O₂ in a microwave oven. After cooling, the digest was filtered and diluted to 25 mL with water.

In the case of soil and sediment samples, amounts of 200 mg were mineralized with 10 mL HNO₃, 2 mL H₂O₂ and 4 mL HF. The same digestion protocol was used in both cases (Table 1). After cooling, the excess of HF in the digest was neutralized by addition of 1 g boric acid, then the digest was filtered and diluted to 50 mL with water. Filtrates were used for the determination of Hg, metals, anions (Cl⁻, F⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻) and residual organic matter which can disturb Hg vapour generation during ultrasonication. To quantify Hg, aliquot volumes of sample in the range 2–1000 μ L were added to 25 mL 0.2 mol L⁻¹ formic acid. The calibration standard solutions (n=6) were prepared by adding aliquot volumes in the range 50–500 μ L of a 10 ng mL⁻¹ Hg stock solution to 25 mL 0.2 mol L⁻¹ formic acid so that the amounts of Hg fall in the range 0–5 ng or 0–0.2 ng mL⁻¹, respectively.

2.3. Instrumentation

The experimental SICV- μ CCP-OES presented in Fig. 1 consisted of a 35 kHz, 140 W Ultrasonic bath SONOREX SUPER RK 102H Bandelin Sonorex (Berlin, Germany), in which the sonoreactor is placed (25 cm³ reaction vessel bubbler), a home-made capacitively coupled plasma microtorch INCDO-2000 (Bucharest, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania), a free running radiofrequency generator of 15x17x24 cm³, Technical University (Cluj-Napoca, Romania) as plasma power source, a home-made gold filament microcollector, Babes-Bolyai University (Cluj-Napoca, Romania) to trap Hg vapour by amalgamation, a Hameg HM 7042-5 power supply Hameg Instruments (Mainhausen, Germany) and a QE65 Pro Spectrometer, Ocean Optics (Dunedin, USA) with 190–380 nm spectral range and 0.4 nm FWHM equipped with a CCD detector cooled at (-20 °C) by a Peltier element. The microspectrometer was mounted on a XYZ translator, which allowed targeting different observation zones by 100 μ m increment in the radially-viewed plasma.²⁹ The collection of the emission signal of Hg at 253.652 nm was achieved using a collimating lens (10 mm focal length) without fiber optic, mounted on the entrance slit of the microspectrometer. This optical arrangement resulted in an improvement of the analytical signal by up to 30% compared to the arrangement with fiber optic.

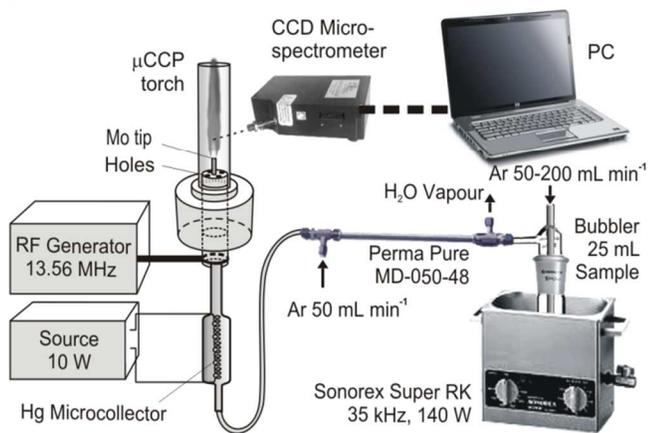
Table 1 Operating conditions for the microwave assisted mineralization of fish and organ tissues, soil and sediment

	Stage				
	1	2	3	4	5
Temperature (°C)	100	160	180	200	100
Hold (min)	5	10	10	10	1
Ramp time (min)	5	5	5	5	1
Power (%) ^a	80	85	85	90	70

^a 100% corresponds to 1450 W

The detector cooling at (-20 °C) provided the decrease of the background emission to less than half compared to the running without cooling.³¹ The ultrasonication causes sample heating along with development of water vapour, which disturbs Hg vapour retention on the gold filament, so that it was necessary to insert a Perma Pure MD-050-48 Nafion membrane tubing, Polypropylene housing material, 120 cm length, Chromoservis (Praha, Czech Republic) to remove moisture. This device can work with a carrier gas flow up to 200 mL min⁻¹ and achieves an efficient removal of water vapour at a Target Dew Point of at least (-8 °C). Under these conditions more than 85% moisture of the carrier gas could be removed without noticeable loss of Hg. The construction of the plasma microtorch was detailed in previous works.^{24,31} Basically, the Ar plasma is sustained at flows of 50–200 mL min⁻¹, power in the range 10–20 W and 13.56 MHz frequency at the tip of a Mo microelectrode, 1.25 mm diameter, 99.95% purity Goodfellow (Cambridge, UK) mounted inside a quartz tube, 5 mm i.d., 25 mm length, 160 nm cut-off, H. Baumbach & Co Ltd. (Ipswich Suffolk, UK). The admission of the Ar stream together with Hg vapour into plasma occurs through four 750 µm diameter channels crossing the microelectrode support on a 3 mm diameter rim. Plasma generated in this way exhibits very good stability at atmospheric pressure and low background emission.

Mercury vapour collection was achieved on a gold coiled-filament (99.95% purity, 100 µm diameter, 23 turns and 46 cm unturned length), Goodfellow (Cambridge, UK) fixed in a quartz capillary of 2.5 mm i.d. and 30 mm length.^{30,32}

**Fig. 1.** Scheme of the SICV-µCCP-OES experimental set-up

The reproducibility of the retention/desorption process of Hg on/from the gold filament was found to be better than 7%, and the direct heating of the filament (5 V, 1.5 A) provided rapid desorption and high flow rate of Hg vapour toward plasma, and hence a high sensitivity.^{30,32}

The comparison method for SICV-µCCP-OES was CV-AFS with chemical Hg CV generation using 20% SnCl₂ solution stabilized in 15% HCl. Determinations were carried out using the fully automated Hydra-AF Mercury Analyzer, Teledyne Leeman Instruments (Hudson, USA). Details about the CV-AFS method, related instrumentation and experimental conditions were given previously.³¹

Metals were determined by inductively coupled plasma optical emission spectrometry using the Spectro CIROS^{CCD} instrument (Kleve, Germany) with axial viewing. Anions were quantified by ionic chromatography using the 761 Compact IC Methrom ion chromatograph (Herisau, Switzerland). The residual organic matter in digest was determined with the N/C 2100 S Analyzer, Analytik Jena (Jena, Germany) with catalytic combustion and non-dispersive IR detector for CO₂ in gas phase. For this purpose, aliquot volumes of sample were brought to pH>2 as recommended by the manufacturer. Sample digestion was performed in the MWS3+Berghof microwave digester (Berghof, Germany) with temperature monitoring option in each vial up to 210 °C. The high pressure in the digestion vials up to 100 atm resulted in an efficient digestion of the biological samples with high content of organic matter.³⁶

2.4. Operation procedure of the SICV-µCCP-OES system

A volume of 25 mL additionally purified 0.2 mol L⁻¹ formic acid was introduced in the sonoreactor to which aliquot volumes of the stock solution of 10 ng mL⁻¹ Hg or digest resulted from CRMs/test samples were added. The purging Ar flow was set to 50–200 mL min⁻¹ and sample was subjected to ultrasonication for a period of up to 10 min at 140 W power level. The Hg vapour generated in the sonoreactor was purged and collected on the gold filament at room temperature. After the Hg trapping step, plasma was turned on, the gold filament was heated by supplying a voltage of 5 V and a current of 1.5 A, and the released Hg vapour was introduced into plasma *via* a 50–200 mL min⁻¹ Ar flow. The Ar flow rate in reverse direction used to remove the water vapour from the Nafion tubing was kept constant at 50 mL min⁻¹. The High Speed Acquisition mode of the QE65 Pro Spectrometer software was started simultaneously with Hg vapour release to record 10 spectral episodes, each with 500 ms integration time.^{24,30,32} The spectra Playback Controls application of the microspectrometer software showed that the Hg emission signal emerged during 2nd–4th episodes, and consequently only the first five episodes were taken into account. The microspectrometer does not allow real-time emission measurements because the CCD detector has lower temporal resolution than a photomultiplier and cannot respond to fast changes of the signal in time. Background correction using the linear two-point model was made for each spectral episode. The total net emission signal at Hg 253.652 nm analytical line resulted from the summation of net episode

spectra in which the Hg emission signal was present. After each run, the sonoreactor vessel was washed several times with ultrapure water. Also, water in the ultrasonic bath was periodically changed because of heating during operation. For decontamination, the sonoreactor vessel was filled from day to day with 10% (v/v) BrCl and rinsed with ultrapure water before using.

3. Results and discussions

3.1. Optimization of the working conditions with the SICV- μ CCP-OES system

Parameters influencing Hg CV generation (formic acid concentration, sonication time, Ar flow rate to purge Hg vapour from the sonoreactor) and those related to plasma microtorch operation (Ar flow rate to sustain plasma, power level and observation height) were optimized to achieve the best analytical performance for Hg determination at 253.652 nm. Each variable was investigated in turn keeping the other variables constant. The influence of the formic acid concentration on CV generation is shown in Fig. 2a, while of the sonication time in Fig. 2b. The maximum emission signal for Hg was observed for 0.2 mol L⁻¹ formic acid. One can see a sharp increase in Hg emission signal up to this concentration after that there is a smooth linear decrease. The enhancement of the signal with formic acid concentration up to 0.2 mol L⁻¹ is due to the increasing yield in the production of reducible species (CO and H₂) upon ultrasonic degradation. The resulted reducible species accomplish further a fast reduction of ionic Hg to elemental species. The decomposition of the formic acid molecule occurs upon ultrasound irradiation by the H and OH reducing radicals arising during sonolitic water decomposition. The decrease of the emission signal for formic acid concentrations higher than 0.2 mol L⁻¹ is attributed to the decrease of sonolysis yield of formic acid and thus of reducing species production caused by the decrease of temperature in the cavitation bubbles. As a consequence, a decrease of the reduction reaction rate of Hg(II) to Hg(0) occurs. Emergence of the Hg emission signal upon ultrasonication even in ultrapure water occurs as a result of Hg(II) species reduction to vapour by radicals like OH and H formed upon water sonication. Details on the kinetics related to sonolysis of formic acid in solution and ultrasound-assisted reduction of Hg(II) species have been published.^{12,13}

An optimum concentration of formic acid established in our method (0.2 mol L⁻¹) lower than that reported by Gil et al. (0.9 mol L⁻¹) in the SI-CVG-GFAAS method is explained by the use in our experiment of an ultrasound bath of higher power and frequency (140 W, 35 kHz) than in the comparative study (100 W, 20 kHz).¹²

The optimal sonication time was found to be 8 min up to which the emission signal increased due to enhancement of Hg vapour amount purged from the sonoreactor and collected on the gold filament. The signal decrease for sonication times over 8 min is caused by the excessive heating of the sample solution,

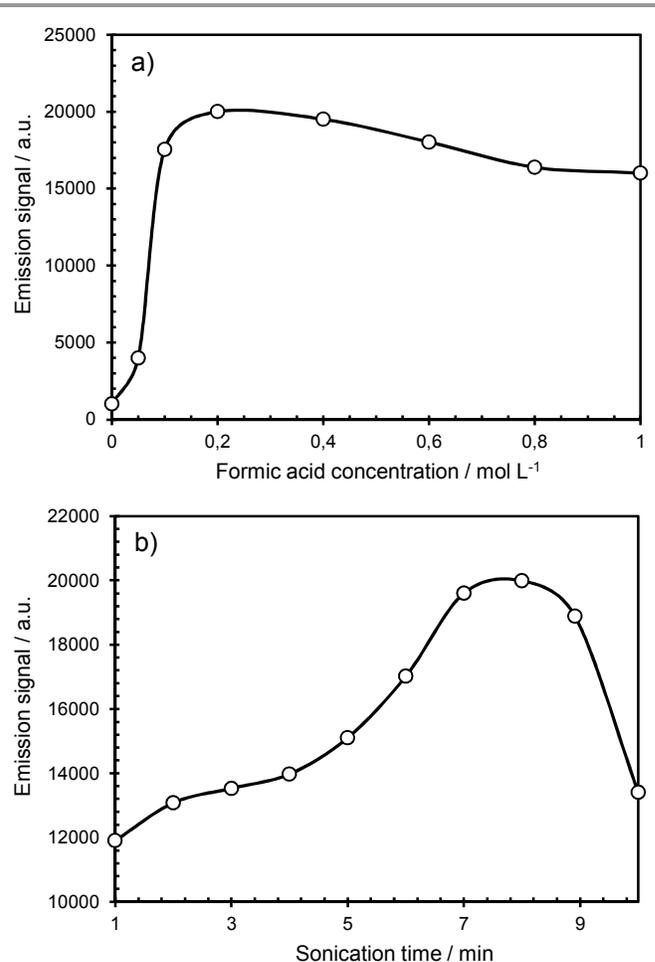


Fig. 2. Effect of parameters influencing SICV generation on the emission of Hg 253.652 nm from 25 mL solution containing 0.4 ng mL⁻¹ (10 ng) Hg. **a.** effect of formic acid concentration for 8 min sonication time; **b.** effect of sonication time in 0.2 mol L⁻¹ formic acid. Other experimental conditions: Ar flow rate to purge Hg and sustain plasma-100 mL min⁻¹; plasma power- 10 W; observation height in plasma- 0.8 mm.

thus generating a higher amount of water vapour that could not be properly eliminated by the Nafion membrane. Indeed, wetting of the Nafion tubing wall was observed. The presence of the water vapour in the gas stream emerging Nafion tubing disturbs Hg vapour retention by amalgamation on the gold filament.

The influence of the Ar flow rate and plasma power on the emission of Hg is presented in Fig. 3a, b. A value of 100 mL min⁻¹ was found to be the best compromise to purge sonoreactor, carry the released Hg vapour from the gold filament and sustain plasma. In this case the outlet dew point is at least (-13 °C) corresponding to a relative humidity of at least 10%, which means that more than 90% of moisture entered together with Ar in the Nafion tubing is removed.

Under these conditions, the optimum observation height was found at 0.8 mm above the Mo tip microelectrode. Although a lower Ar flow rate (i.e. 50 mL min⁻¹) would ensure a dew point of (-20 °C) and a corresponding relative humidity

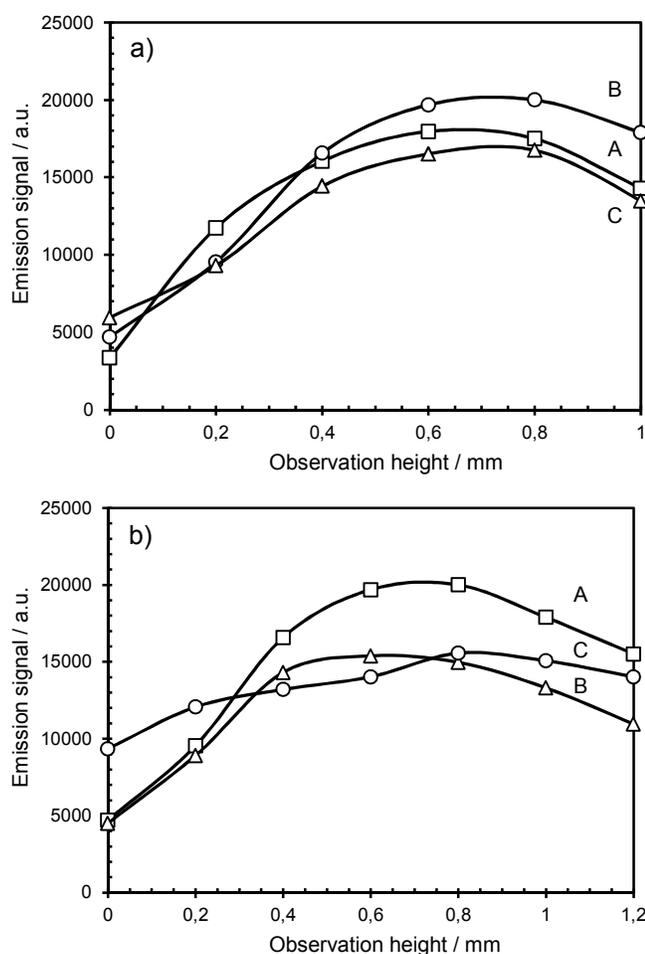


Fig. 3 a. Influence of Ar flow rate (mL min⁻¹) on Hg emission at 10 W plasma power: A – 50; B – 100; C – 150; b. Influence of plasma power (W): A – 10; B – 15; C – 20 at 100 mL min⁻¹ Ar flow rate. Other experimental conditions: formic acid concentration- 0.2 mol L⁻¹; sonication time- 8 min; 25 mL solution containing 0.4 ng mL⁻¹ (10 ng) Hg.

of 5%, it could not be able to provide an efficient purging of Hg vapour during sonolysis.

The operation of the sonoreactor at 200 mL min⁻¹ Ar as maximum value allowed by the Nafion tubing resulted in an inefficient elimination of moisture and drops of condensed water were observed on tubing wall. By this Ar flow rate the outlet dew point is (- 8 °C) and the related relative humidity 15%. On the other hand, the operation of the low power plasma-sonoreactor set-up used in this experiment at Ar flow rates greater than 100 mL min⁻¹ also caused entering of water vapour into the plasma source. Moreover, a greater Ar flow results in shorter residence time of Hg atoms with the same detrimental effect on the excitation process. These considerations explain why the optimum value of 100 mL min⁻¹ Ar flow rate established in this experiment is lower than that previously reported (200 ml min⁻¹) for the procedure using the reduction with SnCl₂-HCl system without sonication, which does not involve solution heating.³⁰

The optimal operation power was found to be 10 W. The decrease of the emission signal as the power increases upon an

efficient removal of water vapour demonstrates that supplemental energy provided to the discharge results in expanding plasma volume rather than increasing excitation efficiency of the analyte atoms.

The effective removal of the water vapour provided the maximum signal at lower power than previously established (20 W) for Hg determination after CV using SnCl₂ and preconcentration on gold filament without drying.³⁰ Thus, the entrance of water droplets into plasma requires supplemental energy to ensure discharge stability.

3.2. Matrix effect

Bendl et al. reported a significant depressive effect from several metals in the upper oxidation state (Cu, Fe and Pb), a lower depressive effect from Zn, Mn and Mg, and an enhancement effect from Co and Ni on Hg determination by CVAAS using UV photoreduction in 3 mol L⁻¹ acetic acid.⁸ Gil et al. remarked depressive interferences by 30% from chloride anion (100 mg L⁻¹ NaCl), 26% from carbonate anion (100 mg L⁻¹ Na₂CO₃), 20% by Co and Zn and 50% by the humic acid on Hg quantification by ET-AAS after SICV generation.¹² Preliminary measurements in our work revealed a drop of the Hg analytical signal by up to 60% when the solution of 0.2 mol L⁻¹ formic acid used for SICV generation contained 5% (v/v) HCl compared to the case when HCl was absent. The depressive effect caused by the chloride ion was only 20% when the concentration of formic acid was increased to 0.4 mol L⁻¹. This raised the hypothesis that the depressive effects could be avoided by increasing the formic acid concentration. However, during the optimization assay it was observed a decrease of the Hg emission signal with the increase of the formic acid concentration attributable to a decrease of the sonolysis rate of formic acid generating reducing radicals. To avoid the time consuming standard addition approach for Hg determination the acid mix used for sample digestion did not contain HCl. Also, no addition of HCl was made to stabilize Hg(II) in digests and calibration standards as was the case in the common chemical derivatization with SnCl₂.^{30-32,35} Instead, Hg was stabilized in 2% (v/v) HNO₃. Sample solutions were appropriately diluted before analysis so that the depressive effects of the matrix containing metals, anions and residual organic matter to be negligible. The method was successfully validated against CRMs. Moreover, results obtained for Hg by the SICV-μCCP-OES method were compared with those found by CV-AFS with conventional cold vapour generation using the SnCl₂-HCl system. The matrix pattern in CRMs and test samples of fish tissue, soil and sediment in the final solution containing 0.2 mol L⁻¹ formic acid is presented in Electronic Supplementary Information (ESI 1 and ESI 2). Sample preparation protocol involving 200 mg soil or sediment mineralized to 50 mL, or 500 mg fish tissue/organs brought to 25 mL and 25–12500 folds subsequent dilution yielded concentration of concomitants which caused no systematic errors.

Table 2. Figures of merit for the determination of Hg by SICV- μ CCP-OES established in 3 successive days

Day	Calibration range (ng) ^a	y- intercept	Slope(signal peak height ng ⁻¹)	r	$s_{y/x}$ ^b	LOD (ng L ⁻¹)	LOD pg
1	0 - 5	139.9	2025.5	0.9995	128.2	4.8	121
2	0 - 5	14.3	2045.2	0.9997	96.6	5.4	134
3	0 - 5	42.2	1949.7	0.9997	94.0	4.9	123
Average	0 - 5	65.5 \pm 66.0	2006.8 \pm 50.4	0.9996 \pm 0.0001	106.3 \pm 19.0	5.0 \pm 0.3	125 \pm 8

^a – 6 calibration points; 0 – 0.2 ng mL⁻¹ Hg in 25 mL

^b – standard deviation of y-residuals calculated using eq. (1)

The high dilution factor (1000–12500) of the analysed samples was necessary to bring Hg concentration in the calibration range rather than eliminate the matrix influence. An accurate determination of Hg by SICV- μ CCP-OES (recovery of 96.3–104.5%) was possible in the presence of (μ g L⁻¹) up to 20 (Cu), 85 (Pb), 40 (Zn), 5800 (Fe), 150 (Mn), 16 (Co), 7 (Ni), 3 (Ag), 30 (Cd), 30 (As), 30 (Cr), anions (mg L⁻¹) 2 (Cl⁻), 2.5 (SO₄²⁻), 2160 (NO₃⁻), 525 (F⁻), 0.3 (PO₄³⁻), and 40 mg L⁻¹ TOC.

3.3. Figures of merit and validation

The figures of merit of the SICV- μ CCP-OES method were obtained under the optimal values of the investigated variables. The characteristics of the calibration curve and the detection limit found in 3 successive days are given in Table 2. The detection limit (3σ criterion) was calculated using the calibration characteristics (LOD = $(3s_{y/x}-y)/m$), where y is intercept and $s_{y/x}$ corresponded to standard deviation of y-residuals calculated as:

$$s_{y/x} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n-2}} \quad (1)$$

The values of \hat{y}_i are the points on the calculated regression line corresponding to the individual x-values and (m) is the slope of the calibration curve.³⁷

The calibration curve over the range 0–5 ng Hg (n = 6) plotted in three consecutive days had the correlation coefficient of 0.9996 ± 0.0001 and slope of 2006.8 ± 50.4 (2.5% standard deviation). These characteristics demonstrate good reproducibility related to Hg purging from solution, Hg collection and release from the gold filament, plasma stability and emission measurement. ESI 3 illustrates an example of successive episodes and total spectrum recorded in 3 consecutive days for a solution containing 0.04 ng mL⁻¹ Hg (1 ng in 25 mL). The dynamic linear range in SICV- μ CCP-OES system was up to 2 ng mL⁻¹ Hg (50 ng in 25 mL) starting from the quantification limit and up to 10 ng mL⁻¹ Hg in CV-AFS.

The detection limit in SICV- μ CCP-OES was found to be 5.0 ± 0.3 ng L⁻¹ or 125 ± 8 pg Hg and allowed quantification of Hg in solution starting from 15 ng L⁻¹. In environmental samples such as soil, Hg could be quantified at concentrations above 375μ g kg⁻¹ considering the digestion protocol and a dilution factor of 100. The limit of quantification in biological samples (fish) was 25μ g kg⁻¹. This detection limit was two times better than previously reported for CV- μ CCP-OES and

CV-AFS using chemical reduction with SnCl₂ (12 ng L⁻¹) without Hg preconcentration.³¹ The method based on SICV and detection by OES using a low power and low Ar consumption plasma microtorch is cost-effective compared to the SnCl₂-HCl common approach and detection by AFS due the much lower reagents consumption.

The detection limit in SICV- μ CCP-OES was much better than that reported by Grede et al. (0.14 μ g L⁻¹) for optical emission spectrometry with cold vapour generation direct current atmospheric pressure glow microdischarge (CVG- μ APGD-OES) generated between a miniature flow He jet nozzle anode and a small-sized flowing liquid cathode or reported by Pohl et al. (0.11 μ g L⁻¹) and Zapata et al. (0.64 μ g L⁻¹) by cold vapour generation microwave microstrip Ar plasma optical emission spectrometry (CV-MSP-OES), using the SnCl₂-HCl reduction system without preconcentration.^{33,38,39} Our detection limit was also better than 2.8 μ g L⁻¹ achieved by Abdul-Majeed et al. by cold vapour dielectric barrier discharge microplasma optical emission spectrometry (CV-DBD-OES).⁴⁰ On the other side, the detection limit in SICV- μ CCP-OES is poorer than 0.08 ng L⁻¹ reported by Yuan et al. in cold vapour atmospheric pressure pulsed direct current microplasma optical emission spectrometry (CV-Pdc-OES) using additional purified SnCl₂ and Hg preconcentration by gold amalgamation.³⁴ It is obvious that Hg preconcentration is mandatory in order to obtain high sensitivity of determination when using microplasmas as emission source. The SICV- μ CCP-OES method involving sonication and on-line preconcentration seems to be time consuming (10 min total time/sample) but provides an excellent limit of detection. The synergistic effect of sonolysis and UV photolysis with nano-TiO₂ catalyst can be exploited to reduce the analysis time.⁵

The proposed method was validated by analysing environmental (soil and sediment) and biological CRMs (fish tissue and organs), than applied on real test samples. The method was also compared to CV-AFS using chemical CV generation with SnCl₂. Results are presented in Tables 3 and 4. Data in Table 3 show good agreement between the results found by SICV- μ CCP-OES and certified values or those found by CV-AFS and SnCl₂-HCl system for chemical derivatization. Recovery of certified values was in the range 96.3–104.5% in SICV- μ CCP-OES and 95.2–109.1% in the method used as reference. The *F test* showed similar precision in the analysis of CRMs and test samples by SICV- μ CCP-OES (0.8–7.0%) and CV-AFS (0.8–10.0%) ($F_{4;4;95\%} = 1-5.06 < F_{\text{tab}} = 6.23$).

Table 3. Results obtained for Hg determination in CRMs by SICV- μ CCP-OES and CV-AFS

Reference material	Certified value \pm U ^a (mg kg ⁻¹)	Found value \pm U ^{a,b} (mg kg ⁻¹)	
		SICV- μ CCP-OES	CV-AFS ^c
CRM04850G	28 \pm 1.13	28 \pm 0.97	28 \pm 0.87
RTC-CRM025-050	99.8 \pm 31.7	99.3 \pm 1.00	99.3 \pm 1.00
LGC6135	3.2 \pm 0.4	3.1 \pm 0.2	3.3 \pm 0.2
LGC6141	1.2 ^d	1.2 \pm 0.06	1.2 \pm 0.03
NCSDC78301	0.22 \pm 0.04	0.23 \pm 0.02	0.24 \pm 0.03
BCR280R	1.46 \pm 0.2	1.44 \pm 0.04	1.39 \pm 0.09
DOLT-4	2.58 \pm 0.22	2.53 \pm 0.07	2.59 \pm 0.09
TORT-2	0.27 \pm 0.06	0.26 \pm 0.01	0.28 \pm 0.02
BCR463	2.85 \pm 0.16	2.82 \pm 0.05	2.83 \pm 0.06

^a – U is expanded uncertainty for 95% confidence level ($U = t_{\text{xs}}/n^{1/2}$)

^b – n = 5 complete dissolution/analysis sequence for each sample

^c – SnCl₂-HCl system

^d – indicative value

Table 4. Comparative results for Hg determination in soil and fish fillet by SICV- μ CCP-OES and CV-AFS

Sample	SICV- μ CCP-OES Mean \pm U ^b (mg kg ⁻¹)	CV-AFS ^a Mean \pm U ^b (mg kg ⁻¹)
Soil		
1.	0.06 \pm 0.002	0.06 \pm 0.002
2.	28.2 \pm 0.5	28.3 \pm 0.6
3.	45.6 \pm 1.7	44.5 \pm 1.5
4.	2.63 \pm 0.05	2.70 \pm 0.07
5.	1.08 \pm 0.07	1.15 \pm 0.06
6.	1.05 \pm 0.06	1.10 \pm 0.05
Fish fillet		
1.	0.12 \pm 0.002	0.12 \pm 0.002
2.	0.14 \pm 0.009	0.15 \pm 0.01
3.	0.17 \pm 0.007	0.18 \pm 0.01
4.	0.21 \pm 0.01	0.22 \pm 0.01
5.	0.18 \pm 0.01	0.19 \pm 0.007
6.	0.11 \pm 0.01	0.10 \pm 0.009

^a – SnCl₂-HCl system

^b – U is expanded uncertainty for 95% confidence level ($U = t_{\text{xs}}/n^{1/2}$) and n = 5 complete dissolution/analysis sequences for each samples

The *t*-test revealed random error between mean results found by the proposed method and certified value ($t_{v=4,95\%} = 0-1.388 < t_{\text{tab}} = 2.776$). Also, no significant differences were identified between results for CRMs and test samples acquired by SICV- μ CCP-OES and CV-AFS ($t_{v=8,95\%} = 0-2.274 < t_{\text{tab}} = 2.306$).

4. Conclusions

It has been demonstrated that SICV using formic acid could be easily interfaced with a low power and low argon consumption μ CCP for Hg determination in various samples by optical emission using a low resolution microspectrometer. The SICV- μ CCP-OES method fulfils most of the demands of green analytical chemistry and has several advantages over conventional reducing approaches as it eliminates expensive reagents (SnCl₂, NaBH₄, HCl) and uses cost-effective miniaturized instrumentation. The method could be used for Hg determination in environmental and biological samples with reasonable precision and accuracy, as an alternative to the conventional CV-AFS using chemical generation of Hg cold

vapour. The interference from transitional metals, anions and organic matter in solution could be eliminated by simple dilution of liquid sample, which allows the use of external calibration. Particular attention should be paid to sample treatment by avoiding HCl because of the significant depressive effect of chloride ion on SICV Hg generation. The concentration of formic acid should be carefully selected as it is a critical parameter. Further study is also needed to shorten the analysis time, i.e. by decreasing the sonolysis period.

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Notes and references

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Electronic Supplementary Information (ESI) available: [ESI 1 Matrix pattern in CRMs of fish tissue, soil and sediment; ESI 2 Matrix pattern in fish and soil test samples; ESI 3 Episodic (A₁-A₃) and total emission spectra (B₁-B₃) of Hg recorded in 3 successive days under the optimum operating conditions in SICV- μ CCP-OES for a solution of 0.04 ng mL⁻¹ Hg (1 ng Hg in 25 mL). Optimal operating conditions: 8 min sonication time; 0.2 mol L⁻¹ formic acid; 10 W plasma power; 100 mL min⁻¹ Ar flow rate; 0.8 mm observation height]. See DOI: 10.1039/b000000x/

References

- C. Bendicho, I. Lavilla, F. Pena-Pereira and V. Romero, *J. Anal. At. Spectrom.*, 2012, **27**, 1831.
- I. Lavilla, V. Romero, I. Costas and C. Bendicho, *TrAC. Anal. Chem.*, 2014, **61**, 1.
- X. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *Anal. Chem.*, 2003, **75**, 2092.
- X. Guo, R. E. Sturgeon, Z. Mester and G. J. Gardner, *Anal. Chem.*, 2004, **76**, 2401.
- Y. G. Yin, J. F. Liu and G. B. Jiang, *TrAC, Trends Anal. Chem.*, 2011, **30**, 1672.
- S. Ribeiro, M. A. Vieira, P. Grinberg and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2009, **24**, 689.
- R. E. Sturgeon and V. T. Luong, *J. Anal. At. Spectrom.*, 2013, **28**, 1610.
- R. F. Bendl, J. T. Madden, A. L. Regan and N. Fitzgerald, *Talanta*, 2006, **68**, 1366.
- J. T. Madden and N. Fitzgerald, *Spectrochim. Acta*, 2009, **64B**, 925.

10. E. Stanisz, J. Werner and H. Matusiewicz, *Microchem. J.*, 2014, **114**, 229.
11. S. Gil, I. Lavilla and C. Bendicho, *Anal. Chem.*, 2006, **78**, 6260.
12. S. Gil, I. Lavilla and C. Bendicho, *Spectrochim. Acta*, 2007, **62B**, 69.
13. E. Hart and A. Henglein, *Radiat. Phys. Chem.*, 1988, **32**, 11.
14. P. Pohl and P. Jamroz, *J. Anal. At. Spectrom.*, 2011, **26**, 1317.
15. Z. Long, Y. M. Luo, C. B. Zheng, P. C. Deng and X. D. Hou, *Appl. Spectrosc. Rev.*, 2012, **47**, 382.
16. Z. Long, C. Chen, X. D. Hou and C. B. Zheng, *Appl. Spectrosc. Rev.*, 2012, **47**, 495.
17. H. Matusiewicz and R. E. Strurgeon, *Appl. Spectrosc. Rev.*, 2012, **47**, 41.
18. X. Yuan, J. Tang and Y. Duan, *Appl. Spectrosc. Rev.*, 2011, **46**, 581.
19. V. Karanassios, *Spectrochim. Acta*, 2004, **59B**, 909.
20. J. A. C. Broekaert, *Appl. Spectrosc.*, 2008, **62**, 227A.
21. Weagant, S. Chen, and V. Karanassios, *Anal. Bioanal. Chem.*, 2011, **401**, 2865.
22. K. K. Moss, K. G. Reinsberg and J. A. C. Broekaert, *J. Anal. At. Spectrom.*, 2014, **29**, 674.
23. T. Iwai, K. Okumura, K. Kakegawa, H. Miyahara and A. Okino, *J. Anal. At. Spectrom.*, 2014, **29**, 2108.
24. T. Frentiu, E. Darvasi, S. Butaciu, M. Ponta, D. Petreus, A. I. Mihaltan and M. Frentiu, *Talanta*, 2014, **129**, 72.
25. X. M. Jiang, Y. Chen, C. B. Zheng and X. D. Hou, *Anal. Chem.*, 2014, **86**, 5220.
26. H. Zheng, J. Ma, Z. Zhu, Z. Tang and S. Hu, *Talanta*, 2015, **132**, 106.
27. P. Jamroz, P. Pohl and W. Żyrmicki, *J. Anal. At. Spectrom.*, 2012, **27**, 1772.
28. I. Mihaltan, T. Frentiu, M. Ponta, D. Petreus, M. Frentiu, E. Darvasi and C. Marutoiu, *Talanta*, 2013, **109**, 84.
29. T. Frentiu, S. Butaciu, M. Ponta, E. Darvasi, M. Senila, D. Petreus and M. Frentiu, *J. Anal. At. Spectrom.*, 2014, **29**, 1880.
30. T. Frentiu, A. I. Mihaltan, E. Darvasi, M. Ponta, C. Roman and M. Frentiu, *J. Anal. At. Spectrom.*, 2012, **27**, 1753.
31. T. Frentiu, A. I. Mihaltan, M. Senila, E. Dravasi, M. Ponta, M. Frentiu and B. P. Pintican, *Microchem. J.*, 2013, **110**, 545.
32. T. Frentiu, S. Butaciu, E. Darvasi, M. Ponta, M. Senila, D. Petreus and M. Frentiu, *Anal. Methods*, 2015, **7**, 747.
33. K. Greda, P. Jamroz and P. Pohl, *J. Anal. At. Spectrom.*, 2014, **29**, 893.
34. X. Yuan, G. Yang, Y. Ding, X. Zhan, Z. Zhao and Y. Duan, *Spectrochim. Acta*, 2014, **93B**, 1.
35. T. Frentiu, S. Butaciu, M. Ponta, M. Senila, E. Darvasi, M. Frentiu and D. Petreus, *Food. Anal. Methods*, DOI: 10.1007/s12161-014-9940-5.
36. T. Frentiu, M. Ponta, E. Darvasi, M. Frentiu and E. Cordos, *Food Chem.*, 2012, **134**, 2447.
37. J.N. Miller and J.C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, 5th Edition, 2005, Pearson Prentice Hall, England.
38. P. Pohl, I. J. Zapata, E. Voges, N. H. Bings and J. A. C. Broekaert, *Microchim. Acta*, 2008, **161**, 175.
39. I. J. Zapata, P. Pohl, N. H. Bings and J. A. C. Broekaert, *Anal. Bioanal. Chem.*, 2007, **388**, 1615.
40. W. S. Abdul-Majeed, J. H. Lozano Parada and W. B. Zimmerman, *Anal. Bioanal. Chem.*, 2011, **401**, 2713.