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Analytical characterization of a method for mercury determination in food using cold vapour capacitively coupled plasma microtorch optical emission spectrometry – compliance with European legislation requirements

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The paper presents the analytical characterization of a high sensitive and inexpensive method for Hg determination in food based on cold vapour capacitively coupled plasma microtorch optical emission spectrometry. The novelty of the work is to combine the on-line preconcentration of Hg cold vapour on a gold filament microcollector with a low-power (20 W) and low Ar consumption (200 mL min^{-1}) microtorch to increase the method sensitivity. The method involves microwave assisted digestion of the lyophilized samples in HNO_3-H_2O_2 mixture, conventional chemical cold vapour generation using the $SnCl_2$-HCl system, on-line preconcentration on a gold filament and emission measurement at 253.652 nm using a low-resolution microspectrometer. The figures of merit were discussed in relation with the demands in the Decisions 2007/333/EC, 2011/836/EC and 2002/657/EC on the determination of toxic elements in food. The detection and quantification limits were 0.005 μg kg^{-1} and 0.015 μg kg^{-1} allowing the use of the method for Hg determination in foods such as chicken meat, bread, rice, vegetables and fruits. For concentrations in the range 0.57-25.2 μg kg^{-1} the precision was 0.7–9.0 %, below the maximum standard uncertainty set in the above mentioned legislation. Recovery of 97.9±4.6 % and trueness in the range (-7.7)-(+4.7 %) in the analysis of five certified reference materials were found to be satisfactory, since the found concentrations fall within the ±10 % bound of the target value. The proposed method developed on miniaturized instrumentation is cost-effective and able to provide Hg determination in food complying with European legislation. The system has analytical potential for the future and prototyping perspectives.

1. Introduction

The development of methods used for the determination of total Hg or its speciation in environmental, biological samples and food is of great interest, due to the extremely high toxicity of both inorganic and organic Hg species.[1-7] The Scientific Panel on Contaminants in the Food Chain of the European Food Safety Authority (EFSA) recommended Hg monitoring in foodstuffs (crops, bread, fruit, vegetables, etc.) other than fish and seafood acknowledged as main contributors to overall exposure.[8] The recommendation was based on data related to Hg content in food collected from 20 European countries over the period 2004-2011. The World Health Organization has set a provisional tolerable weakly intake of 1.6 μg kg^{-1} Hg body weight as methylmercury from fish and seafood and 4 μg kg^{-1} respectively, as inorganic Hg coming from other foods. Frequently, toxic substances, as is the case of Hg, are present in food as traces or ultratraces, so that evaluation of their dietary intake requires analytical techniques of high sensitivity, accuracy and precision.[9] The general requirements concerning the performance of analytical methods and interpretation of results have been set out in Decision (2002/657/EC), while those concerning the methods for the control of Pb, Cd, Hg and inorganic Sn in food in (2007/333/EC) amended by (2011/836/EC). The standardized method for Hg determination in food of animal and vegetable origin is based on cold vapour atomic absorption spectrometry (CV-AAS) from mineralized samples.[10-12] Other methods are cold vapour inductively coupled plasma mass spectrometry (CV-ICP-MS), cold vapour inductively coupled plasma optical emission spectrometry (CV-ICP-OES) and cold vapour atomic fluorescence spectrometry (CV-AFS).[13-17] The ultralow Hg concentration in most food and water samples imposes often a preconcentration step via liquid-liquid extraction, solid-phase extraction, liquid-phase microextraction or retention as amalgam on gold trap.[1-3,6,7] The preconcentration methods based on extraction have some

drawbacks, as they are time consuming, prone to contamination and provide low enrichment factors, while those involving amalgamation are much simpler, fast, offer high enrichment factors, and are suitable for on-line preconcentration. An alternative to these methods could be cold vapour generation from slurry sampling or thermal decomposition/desorption directly from solid matrix and detection by atomic absorption spectrometry.[18,19] Although these methods require minimum sample preparation, they might suffer from low repeatability of measurements due to sample inhomogeneity. A non-chromatographic method based on selective and sequential elution from microcolumn and detection by CV-AAS was reported for mercury speciation as inorganic and methylmercury.[6,7] On-line speciation methods such as anion exchange chromatography and detection by inductively coupled plasma mass spectrometry (HPLC-ICP-MS) and gas chromatography inductively coupled plasma mass spectrometry (GC-ICP-MS) have also been developed.[20,21] Beside classical instrumentation, much attention is currently paid to cost-effective and enough robust miniaturized analytical equipment using atomic spectrometric detection in microplasma sources able to provide good capability in Hg determination after CV generation.[22,23] In line with the global interest for simple, fast, ultrasensitive and relatively green analytical methods using miniaturized instrumentation overcoming the drawbacks related to bulky apparatus, we have developed in our laboratory a miniaturized equipment with capacitively coupled plasma microtorch for optical emission spectrometry (μCCP-OES). This equipment was used for the determination of As and Sb after hydride generation in biodegradable/non-biodegradable materials and soil, simultaneous multielemental analysis of liquid microsamples and Hg determination after chemical cold vapour generation in biodegradable/non-biodegradable materials, water, soil and fish (CV-μCCP-OES).[24-30]

This paper relates on the analytical characterization of a high-sensitive and low-cost method for Hg determination in chicken meat, bread, rice, different vegetables and fruits using the miniaturized CV-μCCP-OES system with Hg preconcentration. The novelty to the previous approach consists of the use the on-line Hg preconcentration in order to improve the detection limit, thus allowing Hg determination in foods other than fish. The on-line preconcentration was performed on a gold filament microcollector followed by Hg desorption by direct heating of the filament connected to a power supply. The figures of merit of the method in terms of limit of detection and quantification, trueness and precision were determined based on the analysis of certified reference materials and various test samples. It was evaluated the compliance of the method performance with the requirements set out in the Decisions 2002/657/EC, 2007/333/EC and 2011/836/EC for analytical methods used in food control. The work is of interest for analytical practice as it put in evidence the possibility to achieve Hg determination in food meeting the requirements of European legislation using a simple equipment.

2. Experimental

2.1. Reagents, standard solution and CRMs

Stock solution of 1000 μg mL^{-1} Hg, 30 % (w/w) HCl ultrapur, 60 % (w/w) HNO_3 ultrapur, 30 % (w/w) H_2O_2 pro analysis, $SnCl_2 \cdot 2H_2O$ pro analysis (<1 10^{-6} % Hg), KBr suprapur and $KBrO_3$ pro analysis purchased from Merck (Darmstadt, Germany) were used. Ultrapure water (18 MΩ cm^{-1} resistivity) obtained in laboratory on a Millipore system (Bedford, USA) was used for the preparation of aqueous solutions. The 20 % (w/v) tin chloride solution stabilized in 15 % (v/v) HCl used as reducing agent was subjected to supplemental purification by purging with Ar for 3 h in ultrasonic field. Potassium bromate was purified by heating at 260 ºC for 12 h in a drying oven. The bromine chloride solution was prepared by dissolving 1.50 g KBr in 100 mL concentrated HCl, after that 1.08 g $KBrO_3$ were slowly added under constant stirring. All glassware, peristaltic pump tubing and cold vapour generation system were cleaned using the 1:9 (v/v) BrCl solution. The Teflon digestion vessels were decontaminated after each run by filling up with 1:9 (v/v) BrCl solution and keeping for 2 h, then empting and rinsing with ultrapure water.

Calibration was performed over the range 0 – 10 ng L^{-1} Hg (n=12) using daily prepared standard solutions stabilized in 5 % (v/v) HCl solution.

Certified reference materials BCR-191 Lyophilized Brown Bread-Trace elements, NIM-GBW-10018 Chicken-Trace elements, NIM-GBW-10019 Apple-Trace elements, IAEA-359 Cabbage-Trace elements, IC-CS-CR-2 Carrot Root Powder-Trace elements, Control sample purchased from LGC Promochem (Wesel, Germany) were analysed to check the accuracy of the method.

2.2. Sample description and preparation

A number of 75 test samples (chicken meat, carrots, celery, parsnips, parsley, tomatoes, peppers, cucumbers, onion, cabbage, potatoes and green salad, apples, pears, peaches, nectarines, grapes, white and brown bread and rice) were subjected to analysis. Most foods were purchased in stores but several samples came from own food production.

All samples were lyophilized, then ground in a mortar and sieved to <100 μm. Next, amounts of 0.2000 g sample were mixed with 10 mL 60 % HNO_3 and 2 mL 30 % H_2O_2, left for preliminary oxidation for 2 – 3 h at room temperature and subjected to microwave digestion using a 4-step temperature program: Step 1: 15 min at 170 ^{0}C and 80 % power; Step 2: 40 min at 200 ^{0}C and 80 % power; Steps 3 and 4: 10 min at 100 ^{0}C and 0 % power. The 100 % power level corresponds to the nominal value of 1450 W. The digests were cooled to room temperature, diluted to 50 mL and stabilized in 5% (v/v) HCl medium.

2.3. Instrumentation

The miniaturized optical emission spectrometer with capacitively coupled plasma microtorch used for the determination of Hg with/without preconcentration onto gold filament microcollector was previously presented.[27-30] Photos of the CV-μCCP-OES experimental system, Hg microcollector and plasma microtorch are provided in Electronic Supplementary Information (ESI). The CV-μCCP-OES experimental set-up consisted of a plasma microtorch–Home-made, INCDO-INOE 2000 Bucharest-Research Institute for Analytical Instrumentation (Cluj-Napoca, Romania), a free-running generator (10 – 30 W, 13.56 MHz, dimensions (LxWxH): 15x17x24 cm^3 as plasma power supply, Home-made, Technical University (Cluj-Napoca, Romania), a QE65 Pro micro-spectrometer, Ocean Optics (Dunedin, USA), a HGX-200 CETAC cold vapour system (Omaha, Nebraska, USA), a gold filament microcollector, Home-made, Babes-Bolyai University (Cluj-Napoca, Romania) and a HM 7042-5 triple power supply, Hameg Instruments GmbH (Mainhausen, Germany) as microcollector power supply. The characteristics of the components were given elsewhere.[27-30]

Table 1 Characteristics of the calibration curve, limit of detection and limit of quantification of Hg by CV-μCCP-OES after on-line preconcentration. Experimental conditions: 20 W plasma power; 200 mL min^{-1} Ar flow rate; 1 mm observation height above tip microelectrode; 8 s acquisition time

Calibration range (ng L^{-1}) [a]	Calibration sensitivity (peak height signal/ng L^{-1})	Correlation coefficient (r)	Limit of detection (LOD)		Limit of quantification (LOQ)[d]	
			(ng L^{-1})	(μg kg^{-1})	(ng L^{-1})	(μg kg^{-1})
0 - 10	1432±18	0.9998	0.02[b]	0.005[c]	0.06	0.015

[a] – n=12 calibration standard solutions
[b] – Obtained after Hg preconcentration from 25 mL sample
[c] – Calculated for 0.2000 g digested sample diluted to 50 mL solution
[d] – Calculated as 3xLOD

The CV-μCCP-OES system with Hg preconcentration on the gold filament microcollector was operated in two steps. In the first step, the Hg vapour generated from 25 mL acidified sample solutions in 5 % (v/v) HCl were trapped on the gold filament microcollector at room temperature. Thus, the sample was fed (3.5 mL min^{-1}) into the HGX-200 and mixed with 20 (w/v) % $SnCl_2$ solution stabilized in 15 % (v/v) HCl (1.0 mL min^{-1}) used as reducing agent. Mercury vapour were swept from the HGX-200 device by an Ar flow of 200 mL min^{-1}. Further, during the thermal desorption step, the gold filament was directly heated for 5 s by supplying a voltage of 5 V and a current of 1.5 A from the HM 7042-5 triple power supply. The direct heating of the filament provided the rapid desorption of Hg and thus a high flow rate of vapour toward plasma ensuring a high sensitivity in Hg determination. The desorbed Hg vapour was introduced into the plasma operated at 20 W and 200 mL min^{-1} Ar flow rate. A number of eleven 3D episodic emission spectra (intensity signal *vs.* wavelength *vs.* time) were recorded for 8 s acquisition time per episode using the High Speed Acquisition mode of the Spectrasuite software. The observation height was 1 mm above the tip microelectrode. The Spectra Playback Controls application showed that the Hg emission signal emerged in the first 2D episode spectrum (intensity signal *vs*. wavelength). The net emission of Hg at 253.652 nm was obtained from the peak height captured during the first episodic spectrum after background correction based on a post-desorption spectrum episode. This approach was possible because the background emission signals remained stable during heating of the microcollector and sample introduction into plasma.

The memory effects were overcome by washing the HGX-200 between samples with 5 % (v/v) HCl for 40 s.

A MW3S+ Berghof model closed-vessel microwave digestion system (Berghof, Germany) with temperature monitoring up to 210 ºC was used for sample mineralization.

2.4. Check compliance of the figures of merit of the CV-μCCP-OES method with the requirements of the European legislation

The figures of merit of the CV-μCCP-OES method were compared with demands in Decisions 2002/657/EC, 2007/333/EC and 2011/836/EC establishing common criteria for the interpretation of test results and the required performance when introducing a new analysis method.

The limit of detection (LOD = $3s_B/m$) was determined according to the 3σ concept using the calibration sensitivity (m) and standard deviation of background (s_B) resulted from10 post-desorption episodic spectra. The limit of quantification (LOQ) was considered as three times the limit of detection. A method for Hg determination in foodstuffs is appropriate if the limits of detection and determination are less than one tenth and one fifth respectively, of the maximum level in Regulation 2006/1881/EC.

The trueness of the determination method was calculated using the relation (1):

$$Trueness = \frac{Found\ value - Certified(indicative) value}{Certified(indicative) value}\ x100 \quad (1)$$

The method trueness is considered acceptable if the found concentrations in the CRMs lie in the limit ±10 % of the target value. It was also verified the compliance of the precision in Hg determination with the performance criterion for foodstuff analysis. Since Horwitz ratio (HorRat), a useful index of method performance with respect to precision, has unacceptable high value for mass fraction lower than 100 μg kg^{-1} Hg, the suitability of the determination method was assessed based on the standard uncertainty of measurement. According to provisions in Decision 2007/333/EC, this value must be lower than the maximum standard uncertainty (U_f) of measurement calculated based on LOD and Hg concentration in samples:

$$U_f = \sqrt{(LOD/2)^2 + (\alpha \times c)^2} \quad (2)$$

where (LOD) is limit of detection in μg kg^{-1} and (α) numeric factor depending on the value of Hg concentration (α = 0.2 for concentrations < 50 μg kg^{-1} Hg).

3. Results and discussions

3.1. Calibration sensitivity, limit of detection and limit of quantification

The characteristics of the calibration curve, limit of detection (3σ criterion) and limit of quantification under the optimal operating conditions of the CV-μCCP-OES system are presented in Table 1.

The Hg preconcentration on the gold filament microcollector resulted in a detection limit of 0.005 μg kg^{-1} and quantification limit of 0.015 μg kg^{-1} allowing the use of the method for Hg determination in vegetables, fruits, various meat, rice and bread. Therefore, the developed analysis method based on CV-μCCP-OES meets the requirements in Decision 2007/333/EC for Hg determination in foodstuff. Compared to the CV-μCCP-OES method without Hg preconcentration with detection/quantification limits of 3/9 μg kg^{-1} applicable only in the analysis of fish tissue, the present approach resulted in a remarkable improvement of the detection capability.[30] In this way, it was possible to quantify Hg at extremely low concentration in many common foods. The limit of detection in CV-μCCP-OES was much better than those reported for traditional methods used for Hg determination with/without preconcentration in biological/food samples. Thus, limits of detection of 2.36 μg kg^{-1}, 0.95 μg kg^{-1} and 80 ng L^{-1} for CV-AAS, 5 ng L^{-1} for CV-AFS, 8 ng L^{-1} or even up to 110 ng L^{-1}

for HPLC-ICP-MS and 3 ng L^{-1} for CVG-ICP-MS were reported .[10,11,13,18,19,20,31] These methods are associated to large and expensive instruments. Those using ICP have elevated operating cost due to high power and Ar consumption (>1 kW, >12 L min^{-1}) compared to a plasma microtorch, such is that under discussion. Thus, a miniaturized, unsophisticated equipment using a plasma microtorch and a low resolution microspectrometer could be used in the future for Hg determination in food with favourable price-performance ratio. The preconcentration of Hg vapour on the gold filament microcollector makes possible the Hg determination in a diversity of samples at extremely low concentration. Also, our procedure is simple, fast and with minimal risk of sample contamination as compared to liquid-liquid extraction procedures.

3.2. Recovery and trueness in Hg determination by CV-μCCP-OES

The results obtained for Hg determination in certified reference materials are presented in Table 2.

Data in Table 2 show a good agreement between found and certified/indicative values for 95 % confidence with recovery in the range 97.9±4.6 %. The determined mean concentrations in the certified reference materials fall within the range (-7.7)–(+4.7) % compared to certified values, so that the CV-μCCP-OES method with Hg preconcentration comply with the requirement in terms of (±10 %) trueness in Decision 2002/657/EC.

3.3. Analysis of real samples

Results obtained for Hg determination in dietary test samples are shown in Table 3.

According to data in Table 3, the overall precision for Hg determination in vegetables, fruits, bread, rice and chicken meat needing Hg preconcentration was between 0.7-9.0 % for concentrations of 0.57-25.2 μg kg^{-1} Hg. The precision of the method fulfilled the requirements for concentrations <25 μg kg^{-1} giving RSD of measurements lower than the limit of 20 % imposed in Decision 2002/657/EC. The standard measurement uncertainty for each sample was lower than (U_f) as seen in Table 3.

4. Conclusions

It was demonstrated that an analytical method based on a miniaturized CV-μCCP-OES laboratory equipment with on-line Hg preconcentration on a gold filament, cost-effective in terms of Ar consumption and plasma power supply, can be successfully used for Hg determination in foodstuffs at extremely low concentration. The introduction of the preconcentration step of Hg resulted in a remarcable enhancement of the detection limit of the method. This was better than those reported for traditional methods based on atomic emission, absorption or fluorescence spectrometry, even that our system included a microspectrometer as detector. The results found in the analysis of certified reference materials and real samples demonstrated compliance of the method with the requirements related to detection/quantification limit, trueness and precision stated in European legislation.

Table 2 Results obtained for Hg determination in Certified Reference Materials by CV-μCCP-OES with on-line preconcentration.
Experimental conditions: 20 W plasma power; 200 mL min^{-1} Ar flow rate; 1 mm observation height above tip microelectrode; 8 s acquisition time

Reference material	M.U.	Certified value±U[a]	Found value±U[a] (n = 5)	Truness[b] (%)
BCR-191 Lyophilized Brown Bread	μg kg^{-1}	2.00[c]	1.95±0.05	-2.5
NIM-GBW-10018 Chicken	μg kg^{-1}	3.6±1.5	3.6±0.1	0
NIM-GBW-10019 Apple	μg kg^{-1}	2.00[c]	1.90±0.02	-5.0
IAEA-359 Cabbage	μg kg^{-1}	13±2	12±1	-7.7
IC-CS-CR-2 Carrot Root Powder	μg kg^{-1}	4.3[c]	4.5±0.2	+4.7

[a] U is expanded uncertainty for 95 % confidence interval.

[b] Calculated as $\frac{Found\ \ value - Certified\ \ value}{Certified\ \ value} \times 100$

[c] Indicative value.

Table 3 Results for the determination of Hg in test food samples by CV-μCCP-OES with on-line preconcentration.
Experimental conditions: 20 W plasma power; 200 mL min^{-1} Ar flow rate; 1 mm observation height above tip microelectrode; 8 s acquisition time

Sample	Sample size	M.U.	Content			s_r[a]	RSD (%)[a]	U_f[b]
			Min	Max	Average			
Chicken meat	6	μg kg^{-1}	2.34	4.42	3.36	0.04-0.08	0.9-3.6	0.47
Carrots, celery, parsnips, parsley	8	μg kg^{-1}	11.0	20.4	15.6	0.2-0.5	0.9-2.9	2.2
Tomatoes, peppers, cucumbers	11	μg kg^{-1}	1.87	3.35	2.40	0.03-0.11	1.3-4.4	0.37
Onion	5	μg kg^{-1}	12.5	15.9	14.3	0.2-0.3	1.3-2.5	2.5
Cabbage	8	μg kg^{-1}	2.23	9.11	5.00	0.06-0.28	0.7-5.3	0.44
Potatoes	5	μg kg^{-1}	10.6	11.7	11.2	0.2-0.3	1.8-2.6	2.2
Black and white grapes	5	μg kg^{-1}	3.18	4.23	3.57	0.05-0.07	0.9-1.9	0.15
Apples, pears, peaches, nectarines	12	μg kg^{-1}	1.25	2.53	1.76	0.03-0.09	1.7-6.0	0.25
White and brown bread	5	μg kg^{-1}	0.57	1.84	1.25	0.04-0.08	3.8-9.0	0.11
Rice	5	μg kg^{-1}	20.0	25.2	22.8	0.2-0.6	0.9-2.2	4.1
Green salad	5	μg kg^{-1}	0.75	2.60	1.70	0.05-0.07	2.0-7.7	0.15

[a] - s_r and RSD – standard deviation and relative standard deviation of repeatability (n=5 complete dissolution/analysis sequences for each sample)

[b] - maximum standard uncertainty of measurement calculated with eq.(2) for the lowest concentration of the range of interest

The investigated system could be considered as a useful analytical instrument for the future with prototyping perspective.

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Electronic Supplementary Information (ESI) available:
a) Components of new CV-μCCP-OES analytical experimental system
b) Hg microcolector with gold filament
c) Capacitively coupled plasma microtorch.
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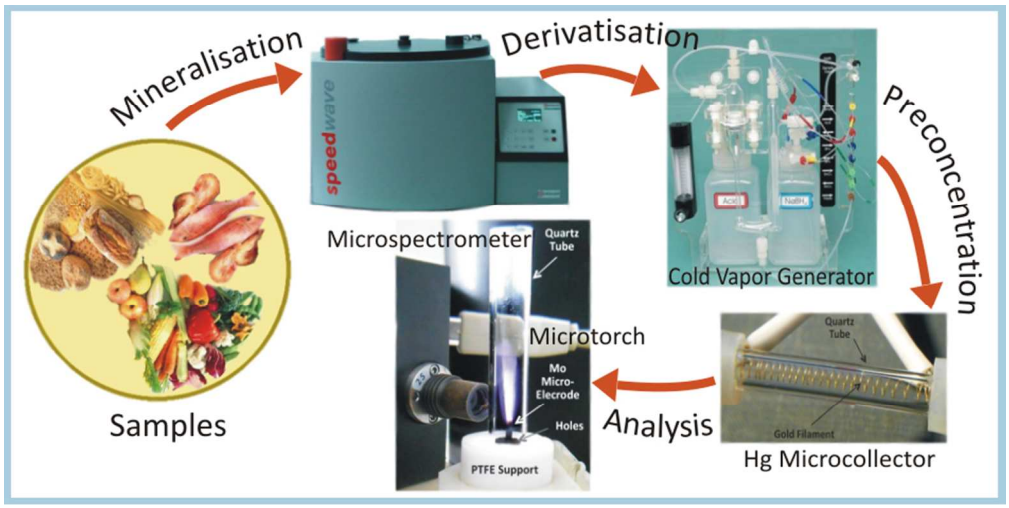

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