Mercury determination in non- and biodegradable materials by cold vapor capacitively coupled plasma microtorch atomic emission spectrometry

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ABSTRACT

A new analytical system consisting of a low power capacitively coupled plasma microtorch (20 W, 13.56 MHz, 150 ml min^{-1} Ar) and a microspectrometer was investigated for the Hg determination in non- and biodegradable materials by cold-vapor generation, using SnCl$_2$ reductant, and atomic emission spectrometry. The investigated miniaturized system was used for Hg determination in recyclable plastics from electronic equipments and biodegradable materials (shopping bags of 98% biodegradable polyethylene and corn starch) with the advantages of easy operation and low analysis costs. Samples were mineralized in HNO$_3$–H$_2$SO$_4$ mixture in a high-pressure microwave system. The detection limits of 0.05 ng ml^{-1} or 0.08 µg g^{-1} in solid sample were compared with those reported for other analytical systems. The method precision was 1.5–9.4% for Hg levels of 1.37–13.9 mg kg^{-1}, while recovery in two polyethylene certified reference materials in the range 98.7 ± 4.5% (95% confidence level).

1. Introduction

Although mercury occurs in the environment at extremely low levels as inorganic (Hg^0, Hg^{2+}) and organic ((CH$_3$)$_2$Hg and CH$_3$Hg$^+$) species it is recognized to be highly toxic for biota as a result of the high bioaccumulation and biomagnification factors. In aquatic medium the inorganic species of Hg^{2+} undergo biomethylation to methylmercury, the form with the greatest toxicity. These features make the mercury to be an element of great interest in terms of both total content and analytical speciation using high sensitive techniques [1–4]. The most common technique for the determination of Hg in liquid samples, emulsions or suspensions uses cold vapor generation (CV) and detection by atomic fluorescence spectrometry (CV-AFS) [5,6], atomic absorption spectrometry in quartz furnace (CV-QFAAS) [7,8] or graphite-furnace (CV-GFAAS) [9–12], inductively coupled plasma atomic emission spectrometry (CV-ICP-AES) [13,14] and furnace atomization plasma emission spectrometry (CV-FAPES) [15]. Cold vapor generation is based on the chemical reduction of Hg species in the acidic sample with SnCl$_2$ [7,13,15] or NaBH$_4$ [10,14] as well as on reagent-free methods such

as electrochemical reduction [6,12], UV photoreduction [8,9,15] or ultrasound irradiation [11]. The sensitivity of the determination can be increased by preconcentration of Hg vapor using out- [7,13–15] or in-atomizer Au/Pd trapping techniques [9–12]. An alternative to CV trapping of Hg vapor is cloud point extraction from aqueous solution in ammonium O,O′-diethyl dithyophosphate (DDTP) in Triton X-114, than CV generation using NaBH$_4$ [16]. Ultra trace amounts of Hg^{2+} and CH$_3$Hg$^+$ species can be determined following concentration by solid-phase microextraction, elution and derivatization [4,17]. A reagent-free method for the determination of total Hg dissolved in natural water with high sensitivity and minimal contamination risk is based on preconcentration by solid-phase microextraction onto catalytic active nano-gold collector, followed by the thermal desorption of species by heating [18,19]. Safavi et al. [20] described a new vapor sensor for Hg in industrial wastewater based on changes in the impedance of single-walled carbon nanotubes induced by the adsorption of CV. A rapid approach for Hg determination was reported to be the direct CV generation by pyrolysis of solid sample followed by spectral detection. The method was used by Geng et al. [5] to determine Hg in coal fly ash, waste incineration ash and soil by CV-AFS and by Resano et al. [21] to quantitate Hg in polymers using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GFAAS).

Several recent papers reported the successful use of microstrip plasma (MSP) [22,23] and cold plasma dielectric barrier discharge (DBD) [24] equipped with miniaturized CCD low resolution spectrometers as specific detectors for Hg. Portable spectrometric equipments with microplasma sources for dedicated analysis ensure easy operation and low running costs compared to the

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traditional laboratory instrumentation [25–27]. Based on these advantages a low power capacitively coupled plasma microtorch (30 W, 13.56 MHz, 0.5 l min^{-1} Ar) was developed in our laboratory and investigated in conjunction with commercially available microspectrometers for the simultaneous multielemental analysis of liquid samples without desolvation by atomic emission spectrometry (μCCP-AES) [28]. The benefits of the system are related to the tolerance of plasma for the introduction of liquid samples by pneumatic nebulization and the relatively simple emission spectrum, which allows the use of low resolution microspectrometers with Full-Width Half-Maximum (FWHM) in the range 0.33–1.5 nm.

The aim of the present study was the evaluation of the μCCP-AES system including the previously presented argon plasma microtorch [28] for Hg determination in non- and biodegradable materials after chemical reduction of Hg^{2+} in solution to cold vapor (CV) with SnCl$_2$. Performances of the CV-μCCP-AES miniaturized system were compared with literature data. The technique was validated by analyzing two certified reference materials of polyethylene and applied for the determination of Hg in recyclable plastics from electronics, and packaging for food and beverages, after microwave assisted acidic mineralization. The content of Hg in such materials is of great interest in relation with recommendations of the European Commission regarding collection of Waste Electrical and Electronic Equipment (2002/96/EC Directive) and Restriction of Hazardous Substances (2002/95/CE and 94/62/CE Directives). These documents stipulate the maximum concentrations of hazardous metals (Hg, Pb, Cd, Cr) in plastics and packaging. In the same time, Hg and its compounds are included in the Frame Work Priority Substances (2008/105/EC Directive).

2. Experimental

2.1. Reagents, standard solution, CRMs and real samples

Stock solution of 1000 μg ml^{-1} Hg, ultrapure 30% (w/w) HCl, 60% (w/w) HNO$_3$, 96% (w/w) H$_2$SO$_4$ and SnCl$_2$·2H$_2$O for Hg determination were procured from Merck (Darmstadt, Germany). The working standard solutions containing 0.2–25 ng ml^{-1} Hg^{2+} stabilized in 5% (v/v) HCl, solutions of 5–25% (w/v) SnCl$_2$ in 5–20% (v/v) HCl were daily prepared.

Throughout the study Milli-Q (18 MΩ cm^{-1}) water obtained in house (Millipore Corp., Bedford, USA) was used. The SnCl$_2$ solution was ultrasonic-purified by Ar purging for 1 h. The glassware was conditioned according to the protocol in ref. [15] involving washing with water followed by leaching for 48 h in 10% (v/v) HNO$_3$ and rinsing with water.

Two polyethylene certified reference materials as granules, ERM-EC 680k and ERM-EC 681k (LGC, Promochem, Wesel, Germany) were used for the validation of the method.

The real samples were plastics based on polyethylene (PE) and acrylonitrile butadiene styrene (ABS) from recyclable electronic equipments, shopping bags of PE and biodegradable materials (corn starch, oxo-biodegradable polyethylene (OPE)) for food packaging and bottles of polyethylene terephthalate (PET) for still and mineral water.

2.2. Instrumentation

The experimental set-up (Fig. 1) is composed of the Ar capacitively coupled plasma microtorch (INCDO-INOE 2000 Bucharest, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania) supplied by the free-running r.f. generator (13.56 MHz, 10–40 W, dimensions 15 × 17 × 24 cm^3) (Technical University Cluj-Napoca, Romania), the HGX-200 hydride generator and cold vapor system (Omaha, Nebraska, USA) and the HR 4000 Microspectrome-
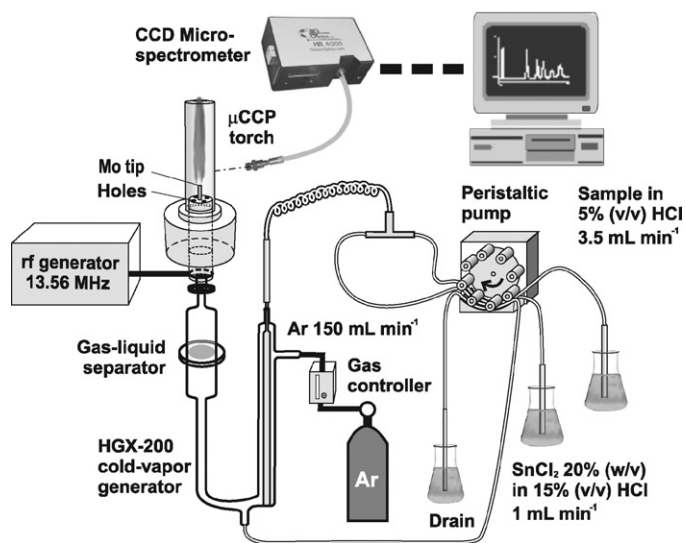

Fig. 1. Schematic of the CV-μCCP-AES system.

ter (200–420 nm spectral range, 3648-element Toshiba CCD-array detector, 0.33 nm FWHM; Ocean Optics, Dunedin, USA).

The emission signal of Hg at 253.652 nm was collected *via* the fibre optic QP 600 μm, 25 cm length (Ocean Optics, Dunedin, USA) and processed by Spectrasuite soft as average of 10 measurements over 5 s integration time. The fibre optic was mounted on a XYZ translator with micrometric adjustment by 0.1 mm increment allowing targeting of different analytical zones in plasma. Coupling between plasma torch and cold vapor generation system was achieved using a PTFE tube.

The flow rates of sample and SnCl$_2$ reducing agent toward the cold vapor generator were 3.5 and 1 ml min^{-1}, respectively. An Ar flow of 100–250 ml min^{-1} (5.0 quality, Linde Gas SRL Timisoara, Romania) was used to purge Hg vapor from effluent and to sustain plasma.

The plasma microtorch used in this experiment and described previously [28] consists of a quartz tube, 25-mm length, 5 mm i.d. (160 nm cut-off, H. Baumbach & Co., Ltd., Ipswich Suffolk, UK) inside which a 1-mm diameter Mo tip microelectrode is mounted. Plasma can be sustained in Ar atmosphere and arises as a diffuse discharge on the tip of the microelectrode connected to the r.f. generator. Argon together with Hg vapor enters the plasma through four 0.75 mm diameter holes drilled in the microelectrode support on a 3 mm diameter circumference. No drying of the Hg cold vapor was necessary. The low operation power does not impose a supplemental cooling of the microtorch assembly besides the Ar flow.

A MWS-3+ Berghof closed-vessel microwave digestor (Berghof, Germany) equipped with temperature monitoring option was used for sample mineralization.

Table 1
Operating conditions for the mineralization of non- and biodegradable materials *via* the microwave digestion system.

	Stage				
	1	2	3	4	5
Temperature (°C)	145	170	190	100	100
Hold (min)	5	10	15	10	10
Ramp time (min)	2	2	2	1	1
Power (%)[a]	80	80	80	0	0

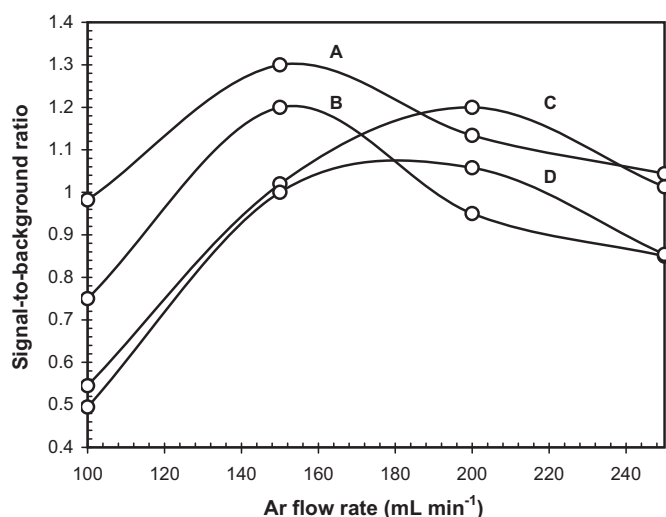[a] 100% power corresponds to 1450 W.

Fig. 2. Signal-to-background ratio in the CV-μCCP-AES system for 2 ng ml^{-1} Hg at 253.652 nm *vs.* plasma power level and Ar flow rate. Power (W): A – 20; B – 25; C – 30; D – 35. Reducing agent: 20% (w/v) SnCl$_2$ in 15% (v/v) HCl.

2.3. Sample treatment

Samples were cut into pieces, washed, air-dried, than ground to grain size <2 mm using a cutting mill. Amounts of 150 mg sample were subjected to mineralization in a mixture of 3 ml 60% HNO$_3$ and 3 ml 96% H$_2$SO$_4$ according to the procedure recommended by the manufacturer of the microwave digestor (Table 1). The digests were diluted to 25 ml and stabilized in 5% (v/v) HCl. Before analysis a 1 + 9 dilution with 5% (v/v) HCl was made.

3. Results and discussion

3.1. Optimization of the working conditions for the CV-μCCP-AES system

The CV-μCCP-AES system was independently optimized both in terms of chemical and instrumental conditions to obtain the maximum spectral response for a 2 ng ml^{-1} Hg^{2+} solution in 5% (v/v) HCl. The optimal condition for CV generation corresponded to a concentration of 15% (v/v) HCl in the solution of the SnCl$_2$ reducing agent. The dependence of the Hg emission on SnCl$_2$ concentration in 15% (v/v) HCl emphasized a limitation of the signal for concentrations greater than 20 (w/v)% of the reducing agent.

The working conditions in μCCP-AES were optimized for the highest signal-to-background ratio (SBR) in respect with plasma power and Ar flow rate (Fig. 2).

According to data in Fig. 2, the working conditions selected for plasma were 20 W power level and 150 ml min^{-1} Ar flow. The observation height is another critical parameter as demonstrates the variation of SBR over height in Fig. 3.

The optimal viewing height for Hg determination in the plasma developed under the previously mentioned conditions was found to be 1.5 mm above the tip microelectrode.

3.2. Figures of merit

The calibration curve $y = (12 \pm 15) + (368 \pm 8)c$ ($n = 12$; 95% confidence interval) over the concentration range 0.2–25 ng ml^{-1} Hg had 0.999 correlation coefficient and 1% relative standard deviation of the slope proving both good linearity and stability of the emission signal. The detection limit of 0.05 ng ml^{-1} Hg (3σ criterion) was estimated based on the SBR value of 1.3 for a solution of 2 ng ml^{-1} Hg and the 1% relative standard deviation of background
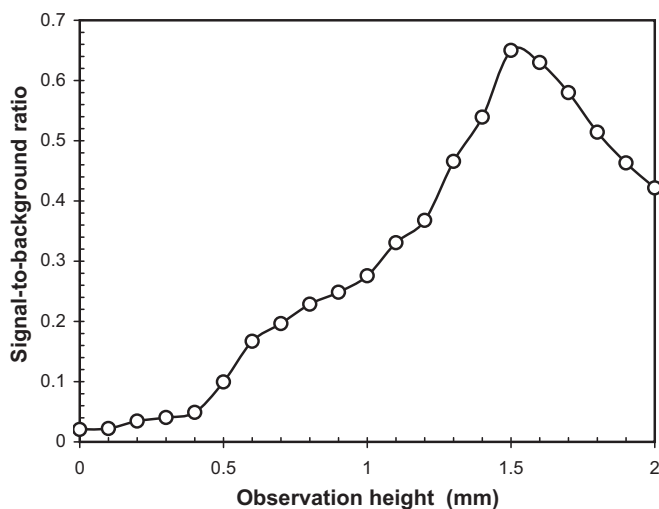
Table 2
Limit of detection (LOD) (3σ criterion) of mercury by CV-μCCP-AES compared to other analytical systems.

Technique	Conditions	LOD (ng ml^{-1})	LOD (μg g^{-1})	Samples	Ref.
CV-μCCP-AES	20 W; 150 ml min^{-1} Ar; HR 4000 microspectrometer with CCD; SnCl$_2$; without amalgamation	0.05	0.08[a]	Plastics and biodegradable materials	This work
CV-ICP-AES	1200 W; >15 l min^{-1} Ar; NaBH$_4$; without amalgamation	0.07–0.12	0.05–0.09	Fish fillet, pig kidney and environmental materials	[14]
CV-FAPES	70 W; 250 ml min^{-1} He support plasma and 40 ml min^{-1} He carrier for CV; SnCl$_2$; UV reduction; without/Au amalgamation	0.25/0.05	–	River water	[15]
CV-MSP-AES	10–40 W; 50–1000 ml min^{-1} Ar; USB 2000 microspectrometer; SnCl$_2$; Au amalgamation	0.05	0.93	Soil	[22]
	40 W; 15 ml min^{-1} Ar; USB 2000 microspectrometer; SnCl$_2$; without amalgamation	0.64	–	Domestic and lake water	[23]
CV-LS-QFAAS	Quartz atomizer; reagent-free: UV photoreduction; without amalgamation	2.1	0.105	Dogfish liver	[8]
	Quartz atomizer, 125 ml min^{-1} Ar; SnCl$_2$ or NaBH$_4$; without amalgamation	0.06–0.19	0.005–0.016	Fish fillet	[13]
CV-LS-GFAAS	Reagent-free: UV photolysis; in-atomizer trapping onto Pd coated graphite furnace	0.12	–	–	[9]
	NaBH$_4$; graphite furnace; in-atomizer trapping on Au-gauze	0.002–0.005	0.001–0.005	Fish fillet	[10]
	Reagent-free: Sono-induced cold vapor in formic acid, in-atomizer trapping onto noble metal-pretreated platform	0.03	–	Natural water	[11]
HR-CS-GFAAS/LS-GFAAS	Direct solid sampling; primary continuum source (Xe lamp)/line source (LS)	–	0.6/2.2	Plastics	[21]

[a] 150 mg sample dissolved in 25 ml and subsequent 10 fold dilution with 5% (v/v) HCl.

Fig. 3. Signal-to-background ratio for 1 ng ml^{-1} Hg at 253.652 nm in CV-μCCP-AES *vs.* viewing height for 20 W plasma power and 150 ml min^{-1} Ar. Reducing agent: 20% (w/v) SnCl$_2$ in 15% (v/v) HCl.

(n = 10). The raw spectrum of Hg for concentrations of 0.2, 0.5 and 1 ng ml^{-1} under the optimum chemical and instrumental conditions and that resulted after background correction were recorded in order to validate the detection limit (Fig. 4). Background correction was made by subtracting from the raw spectrum that of the blank solution of 5% (v/v) HCl and 20% (w/v) SnCl$_2$ in 15% (v/v) HCl as reducing acid.

The detection limit expressed in dry mass considering the sample preparation protocol was 0.08 μg g^{-1}. Consequently the quantitation limit of 0.25 μg g^{-1} Hg by CV-μCCP-AES allows Hg determination in recyclable plastics even without preconcentration, since the normal values in such materials exceed this concentration [29]. Table 2 provides a comparison of Hg detection limit by CV-μCCP-AES with those reported in other analytical systems using the CV generation.

Form the point of view of analytical capability, the detection limit of Hg in CV-μCCP-AES is similar or better than in other analytical systems such as CV-ICP-AES and quartz furnace atomic absorption spectrometry without preconcentration. An advantage of the instrumentation under study over the laboratory systems using ICP for Hg determination is the significantly reduced maintenance cost following the much lower Ar demand for μCCP. Unlike in MSP and DBD microplasmas, the Hg vapor should not be dried before introduction into μCCP. Generally, the presence of water vapor in the support gas of microplasmas results in the instability of the discharge and the decrease of the emission signal of mercury.

When comparing with quartz/graphite furnace atomic absorption spectrometry using out- or in-atomizer trapping, the detection limit in CV-μCCP-AES is higher up to one order of magnitude. On the other side, our detection limit is better than in HR-CS-GFAAS/LS-GFAAS with direct generation of vapor from solid, probably as a result of the limited amount of sample that can be subjected to the analysis.

3.3. Chemical analysis

Results obtained for low and high concentration of Hg in two CRMs of polyethylene are presented in Table 3.

The average recovery of 98.7 ± 4.5% for 95% confidence interval demonstrates that the CV-μCCP-AES provides reliable results for Hg determination in plastics. In the same time, the approach using the HNO$_3$–H$_2$SO$_4$ mixture provides a good mineralization of the sample.
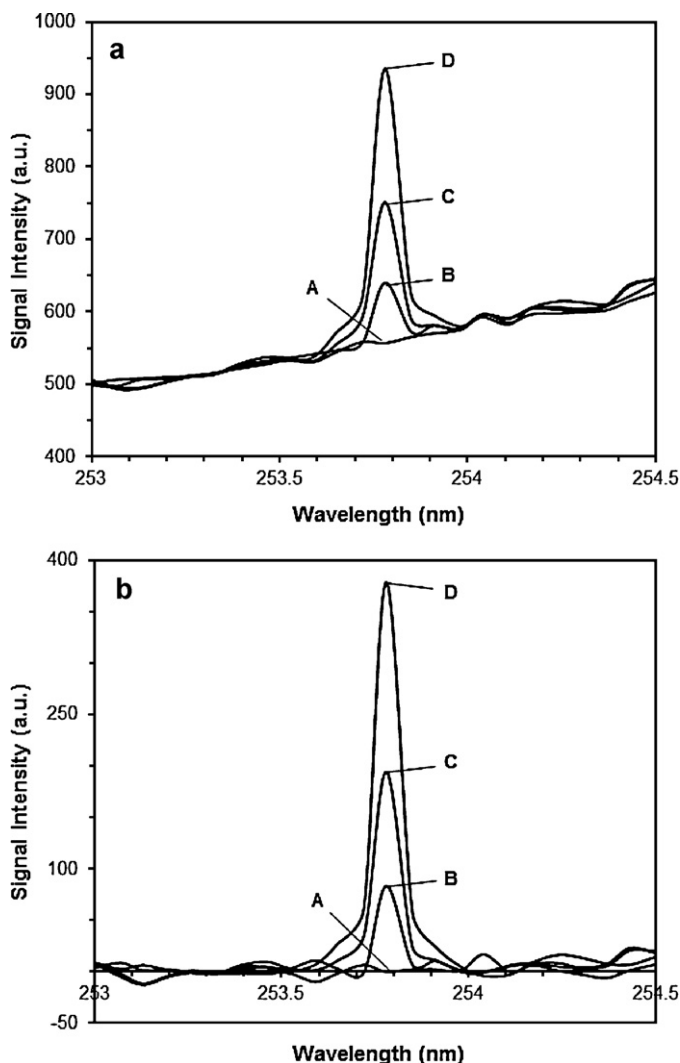

Fig. 4. Raw emission spectrum (a) and spectrum after background correction (b) of Hg at 253.652 nm. Experimental conditions: 20 W plasma power; 150 ml min^{-1} Ar; 1.5 mm observation height; 20% (w/v) SnCl$_2$ reducing agent in 15% (v/v) HCl. A – blank solution 5% (v/v) HCl; B – 0.2 ng ml^{-1} Hg; C – 0.5 ng ml^{-1} Hg; D – 1 ng ml^{-1} Hg.

Results obtained for Hg determination in real samples of non- and biodegradable materials are shown in Table 4.

For amounts in the range 1.37–13.9 mg kg^{-1} Hg the overall precision of the determination was 1.5–9.4%. According to data in Table 4, the Hg concentration in non-biodegradable materials (mainly ABS) was higher than in those biodegradable. In the latter, the lower levels corresponded to materials containing corn starch. Although the found values are below those imposed by the EU Directives, the question remains whether high amounts of such materials, namely those biodegradable, on landfill represents a risk for environment, as remarked by other authors [29]. The answer could result from a leaching test in water, which is under consideration.

Table 3
Results for Hg determination (n = 5) by CV-μCCP-AES in certified reference materials of polyethylene.

CRM	Certified value ± U[a] (mg kg^{-1})	Found ± U[a] (mg kg^{-1})
ERM-EC 680k	4.64 ± 0.20	4.58 ± 0.22
ERM-EC 681k	23.7 ± 0.8	23.4 ± 1.0

[a] U, extended uncertainty (95% confidence level).

Table 4
Results for the determination of Hg in non- and biodegradable materials by CV-μCCP-AES.

Material	Sample size	Content (mg kg^{-1})			s_r (%)[a]
		Min	Max	Average	
ABS[b]	10	6.46	13.9	9.00	1.5–3.2
PE[c] shopping bag	10	1.39	5.22	3.53	2.4–9.4
Biodegradable materials[d]	10	2.01	5.91	3.93	2.1–3.3
PET[e] still/mineral water	10	1.37	6.80	3.20	5.1–7.1

[a] Relative standard deviation of repeatability ($n = 5$).
[b] Acrylonitrile butadiene styrene from personal computers.
[c] Polyethylene.
[d] Shopping bags of (oxo-)biodegradable polyethylene (OPE) or corn starch.
[e] Bottles of polyethylene terephthalate.

4. Conclusions

It has been demonstrated that a miniaturized analytical system consisting of an Ar capacitively coupled plasma microtorch equipped with a CCD microspectrometer is a viable alternative to classical laboratory systems for the Hg determination in non- and biodegradable materials. The detection limit achieved in CV-μCCP-AES was similar or better than in other analytical systems without preconcentration by amalgamation. Moreover the use of inexpensive equipment complying with the analytical demands for a dedicated determination, which is the case of Hg, is more advantageous. Thus, the analytical system with μCCP has the advantage of easy operation, low Ar consumption to sustain plasma and substantially reduced analysis costs. The proposed system can be implemented in the control of plastic materials used in the electronic industry or within centers of collecting and recycling plastics. The small modular design of the analytical system is a prerequisite for extension of in situ measurement applications when sample processing is not required.

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