



New method for mercury determination in microwave digested soil samples based on cold vapor capacitively coupled plasma microtorch optical emission spectrometry: Comparison with atomic fluorescence spectrometry



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ABSTRACT

A new sensitive method for total mercury determination in digested soils using a miniaturized analytical system based on cold vapor capacitively coupled plasma microtorch optical emission spectrometry was developed and compared with cold vapor atomic fluorescence spectrometry as the standardized method. The soil samples were subjected to microwave digestion in aqua regia, than Hg cold vapor were chemically generated with SnCl₂ and introduced via a 150 ml min⁻¹ Ar flow rate in the plasma microtorch operated at 10 W power level. The optical emission signal at 253.652 nm was measured with a commercially available microspectrometer. The method detection limit was 4.8 µg kg⁻¹ Hg, similar to that obtained in the standardized reference method. The precision of Hg determination over the concentration range of 0.27–55 mg kg⁻¹ was 0.8–7.7%. Analysis of six CRMs revealed a recovery of 97 ± 7% similar to 97 ± 9% found in the method based on cold vapor atomic fluorescence spectrometry. The Bland and Altman test carried out on 31 test soil samples showed no significant statistical difference between the results obtained by the proposed method and that taken as reference. The investigated analytical system can be prototyped as an alternative for the commercially existing atomic fluorescence spectrometry instrumentation. The benefits of the system are related to small size instrumentation and low analysis cost due to the low power and low Ar consumption for plasma generation.

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1. Introduction

Determination of mercury is an important current issue as even at low concentration it is one of the most toxic elements with general impact on the ecosystem and human health. Mercury occurs in the environment by both natural and anthropogenic sources. The anthropogenic origin is related to the combustion of coal and fuel oil, incineration of municipal and medical wastes, other industrial processes such as manufacture of metals, chlor-alkali, explosives, cement and fertilizers. The natural sources of Hg include mainly volcanoes and forest fires. The mercury content in soil ranges generally between 0.003 and 4.6 mg kg⁻¹, with a mean value of 0.5 mg kg⁻¹, while in contaminated areas concentrations up to 11,500 or 14,000 mg kg⁻¹ have been reported [1–4]. In soil, the inorganic (Hg²⁺) species can be converted to methylmercury species (CH₃Hg⁺) of high toxicity and mobility or precipitated as sulfide [5,6]. Both Hg²⁺ and CH₃Hg⁺ are

highly mobile, non-biodegradable and bio-accumulative, and can enter the food chain by the seafood, crops and vegetable.

The spectrometric methods for the determination and monitoring of total Hg and its species are periodically reviewed [7–11]. Two major routes are available to determine Hg in soil, sediment, airborne particulate matter and mine wastes, involving either direct determination from solid sample or cold vapor (CV) generation after acidic digestion. The direct methods are based on thermal desorption atomic absorption spectrometry (TD-AAS) with/without gold amalgamation [12–15], X-ray absorption near edged spectroscopy (XANES) and micro X-ray fluorescence (µXRF) [16], and extended X-ray absorption fine structure spectroscopy (EXAFS) [17]. In the category of direct methods can be included the CV generation performed on slurry materials combined with atomic or mass spectrometric detection, recently reviewed for the first time [18]. The direct methods for Hg determination in solid sample have several advantages such as rapidity, no need for intensive sample treatment, low risk of analyte loss by volatilization and the opportunity of using aqueous calibration. Some drawbacks are related to the factors influencing the Hg release from the solid by thermal desorption or CV generation, such as sample inhomogeneity, particle size,

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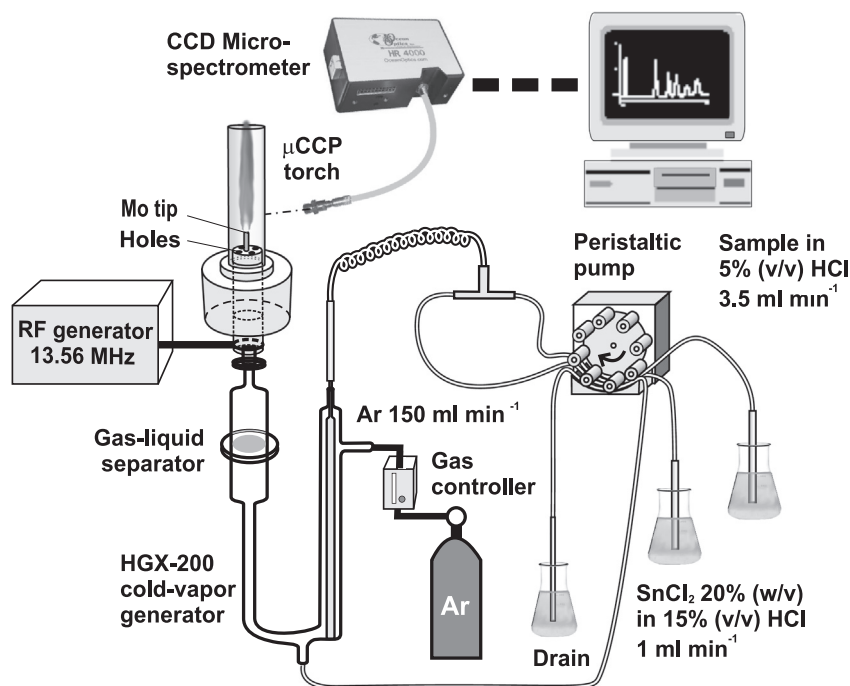


Fig. 1. Schematic of the CV- μ CCP-OES set-up.

nature of species and sample matrix. Therefore, there is a tendency to use the method of standard additions to eliminate possible matrix effects and ensure the accuracy of results. More convenient from this point of view are the methods involving Hg CV generation using either SnCl_2 or NaBH_4 from the digested sample and detection by atomic fluorescence spectrometry (CV-AFS) [14,19], atomic absorption spectrometry (CV-AAS) [20] or inductively coupled plasma mass spectrometry (CV-ICP-MS) [21]. A strategy to avoid the polyatomic interferences in CV-ICP-MS was the microwave induced sample combustion, then mercury separation by absorption in an acidic solution followed by CV generation [22]. Guo et al. [23] reported a method to determine Hg in soil and sediment by ICP-MS using O_2 as the reaction gas in the dynamic reaction cell technology in order to overcome the severe tungsten oxide interference. Huang et al. [24] developed a new method for Hg speciation as inorganic and organic forms using AFS and UV-induced atomization of gaseous hydrides after post-column derivatization of Hg species separated by high performance liquid chromatography.

Currently, the development of new, robust and inexpensive spectrometric methods allowing Hg determination at $< \text{ng l}^{-1}$ level after reagent-free CV generation and preconcentration is of great interest. In this context it should be emphasized the analytical method based on direct solid phase microextraction of Hg species from natural water onto catalytically nanogold collector, followed by thermal desorption and AFS detection (SPME-AFS), which requires neither complexation

nor derivatization [8,25–27]. The development of spectrometric methods and miniaturization of instrumentation based on microplasma sources for spectrochemical analysis of elements after hydride or CV generation have become a field of innovation in recent years [28–31]. The miniaturized plasma torches have simpler construction, run at low Ar/He flow and can be integrated in portable systems using microspectrometers suitable for *in-situ* determination of elements. In line with this trend, Cervený et al. [32] determined Hg in water samples by electrochemical CV generation coupled to microstrip microwave induced He plasma optical emission spectrometry. In our laboratory a method for Hg determination in non- and biodegradable materials by cold vapor capacitively coupled plasma microtorch optical emission spectrometry (CV- μ CCP-OES) using a low resolution microspectrometer as detector was developed [33]. The same inexpensive and robust analytical system was used for Hg determination in bottled water with a detection limit of 0.02 ng l^{-1} after vapor preconcentration on a gold filament microcollector [34]. Preliminary studies have demonstrated that our plasma microtorch is an appropriate excitation source for the multielemental analysis by optical emission at the resonance lines [35].

The focus of this article is on the development and evaluation of an inexpensive method based on CV- μ CCP-OES for the determination of total Hg in soil as an alternative to the CV-AFS method applied on commercially available instrumentation [36]. A performance study [37,38] was carried out to validate and characterize the proposed

Table 1
Characteristics and operating conditions for the CV- μ CCP-OES system.

Component	Operating conditions
Plasma microtorch (Home-made, INCDO-INOE 2000 Bucharest, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania)	Capacitively coupled with tip microelectrode of Mo (1.25 mm diameter) mounted in a Mo support inside a quartz tube (25 mm length, 5 mm i.d. and 160 nm cut-off; H. Baumbach & Co, Ltd., Ipswich Suffolk, UK). Argon inlet (150 ml min^{-1}) in plasma together with Hg vapor through four 0.75 mm diameter channels crossing the microelectrode support on a 3-mm diameter rim. Plasma power in this study: 10 W.
Plasma power supply (Technical University, Cluj-Napoca, Romania)	Free-running generator (13.56 MHz, 10–40 W), small size ($L \times W \times H: 15 \times 17 \times 24 \text{ cm}^3$)
Ocean Optics Microspectrometer (Dunedin, Florida, USA)	QE65 Pro (190–350 nm spectral range, FWHM 0.4 nm, back-illuminated TE Cooled ($-20 \text{ }^\circ\text{C}$) Hamamatsu Detector S7031-1006S.
CETAC hydride/cold vapor system (Omaha, Nebraska, USA)	HGX-200 model equipped with a 4-channel peristaltic pump. Sample flow rate: 3.5 ml min^{-1} ; SnCl_2 solution flow rate: 1 ml min^{-1} .
Data acquisition and signal processing	SpectraSuite software, background correction. Integration time: 10 s

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