

Evaluation of Five Phase Digitally Controlled Rotating Field Plasma Source for Photochemical Mercury Vapor Generation Optical Emission Spectrometry

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A new sensitive method for total mercury determination in reference materials using a 5-phase digitally controlled rotating field plasma source (RFP) for optical emission spectrometry (OES) was developed. A novel synergic effect of ultrasonic nebulization (USN) and ultraviolet-visible light (UV-Vis) irradiation when used in combination was exploited for efficient Hg vapor generation. UV- and Vis-based irradiation systems were studied. It was found that the most advantageous design was an ultrasonic nebulizer fitted with a 6 W mercury lamp supplying a microliter sample to a quartz oscillator, converting liquid into aerosol at the entrance of the UV spray chamber. Optimal conditions involved using a 20% v/v solution of acetic acid as the generation medium. The mercury cold vapor, favorably generated from Hg²⁺ solutions by UV irradiation, was rapidly transported into a plasma source with rotating field generated within the five electrodes and detected by digitally controlled rotating field plasma optical emission spectrometry (RFP-OES). Under optimal conditions, the experimental concentration detection limit for the determination, calculated as the concentration giving a signal equal to three times the standard deviation of the blank (LOD, 3σ_{blank} criterion, peak height), was 4.1 ng mL⁻¹. The relative standard deviation for samples was equal to or better than 5% for liquid analysis and microsampling capability. The methodology was validated through determination of mercury in three certified reference materials (corresponding to biological and environmental samples) (NRCC DOLT-2, NRCC PACS-1, NIST 2710) using the external aqueous standard calibration techniques in acetic acid media, with satisfactory recoveries. Mercury serves as an example element to validate the capability of this approach. This is a simple, reagent-saving, cost-effective and green analytical method for mercury determination.

Keywords Rotating field plasma, photochemical vapor generation, optical emission spectrometry, mercury determination

(Received May 21, 2014; Accepted June 2, 2015; Published October 10, 2015)

Introduction

Determination of mercury is an important current issue because even at low concentrations, it is one of the most toxic elements with a general impact on the ecosystem and human health. Most of the mercury in environmental and biological systems is in the form of inorganic mercury salts and organic forms of mercury (e.g. methylmercury).¹ Thus, the need for the development and validation of analytical methodologies for the determination of mercury in environmental and biological materials has been urgent in recent years.

Mercury has been traditionally determined using cold vapor generation coupled to analytical techniques such as atomic absorption spectrometry (CV-AAS), fluorescence spectrometry (CV-AFS), inductively coupled plasma optical emission spectrometry (CV-ICP-OES), microwave induced plasma optical emission spectrometry (CV-MIP-OES) and inductively coupled plasma mass spectrometry (CV-ICP-MS).^{2,3} In general, these

methods are simple and free of interferences. In the main vapor generation methods (as cold vapor and hydride generation) several reductants have been investigated for the reduction of mercury species Hg²⁺ to the elemental form Hg⁰, with the most frequently adopted method involving the use of sodium (or potassium) tetrahydroborate (THB)⁴ and stannous chloride.⁵

Determination of mercury utilizing cold vapor generation (CVG) requires a large amount of concentrated chemical reductants causing contamination of analyzed samples and forming a large amount of gaseous by-products and waste. The solution to these problems is to reduce Hg²⁺ to Hg⁰ using UV irradiation and/or ultrasound in the presence of low molecular weight organic compounds. This method helps decrease the consumption of relatively expensive and/or unstable chemical reductants such as tetrahydroborate and limit the amount of waste, making this method less costly and “greener” than traditional chemical vapor generation, as illustrated by recent review articles.⁶⁻⁹ On the other hand, the direct use of visible light irradiation (UV light, the sun) for sample pre-treatment represents a sustainable technique for sample preparation that does not consume large quantities of chemicals or energy.^{10,11}

Currently, the development of new, robust and inexpensive

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Table 1 Characteristics and operating conditions for the developed USN-UV/Vis-CVG-RFP-OES systems

<i>Optical emission spectrometer</i>	
Mounting	Czerny–Turner in tetrahedral set-up
Focal length/mm	500
Spectral range/nm	193 – 852
Order lines	28th – 123rd
<i>RFP-OES parameters</i>	
Operating frequency/kHz	20 – 100 (fixed at 60)
Field rotation frequency/kHz	4 – 20 (fixed at 12)
Forward power/W	200
RFP head	5-phase rotating field digitally controlled plasma, water cooled.
Poly-phase plasma generator power/W	250 (Ertec, Wrocław, Poland) -modified
Open circuit voltage (OCV)/kV	4
Pulse-width, %	10 – 90, tunable
Signal waveform	Rectangular
Turns ratio of the output transformers	1:12
Output transformers total leakage inductance (referred to the primary)/mH	1.3
Plasma viewing mode	Axial
Plasma form	Planar
Plasma torch	Quartz tube, 3.0 mm i.d., air cooled
Helium flow rate/mL min ⁻¹	200
<i>OES data acquisition</i>	
Read	On-peak
Integration time/s	0.1
Background correction	Fixed point
Measurement mode	Peak height
Analytical wavelength/nm (line type)	Hg 253.652 (I)

spectrometric methods allowing Hg determination at < ng L⁻¹ level after reagent-free CV generation is of great interest. Plasma sources including microwave plasmas (MWPs) have played an important role as radiation/ionization sources for atomic and molecular spectrometry.¹²⁻¹⁴ The argon or helium microwave induced plasma (Ar-MIP or He-MIP) is commonly sustained at the atmospheric pressure in one-tube quartz or ceramic torches using cylindrical Beenakker resonant cavities, *e.g.*, operated in TM₀₁₀ modes, and surfactants. In recent years, compact helium plasma sources operating at atmospheric pressure have been of great importance in optical emission spectrometry (OES) as well as in mass spectrometry (MS). Among other plasma sources, some interesting multi-electrode approaches of plasma powered by rotating fields have been reported, operating under different regimes including electrode arrangement and operating conditions such as power, frequency and gas flow.¹²⁻¹⁷ Jankowski *et al.* demonstrated that rotating field discharges operating at the kHz level could be analytically useful for determination of gaseous samples.^{16,17}

In the present work, a novel, on-line hyphenated system based on ultrasonic nebulization and photo-induced chemical vapor generation with digitally controlled rotating field plasma-optical emission spectrometry was developed and evaluated for the determination of mercury (USN-UV-CVG-RFP-OES). A further simplification of the methodology is attained when acetic acid is added as a precursor of reducing species upon UV irradiation. A performance study was carried out to validate and characterize the proposed method in terms of limit of detection, precision and accuracy by analyzing certified reference

Table 2 Operating conditions for the developed photo-induced USN-CVG systems

<i>Dual-mode capillary ultrasonic nebulization parameters</i>	
Instrument	Dual mode ultrasonic nebulizer without desolvation system
Solution flow mode	Continuous
Transducer frequency/MHz	1.65
Acoustic power/W	45
Transducer type	Piezo-electric quartz plate, water cooled
Spray chamber	Cyclonic
Nebulizer gas (He) flow/mL min ⁻¹	200
<i>UV photo-assisted vapor generation (SYSTEM A)</i>	
Power of UV pen lamp/W	6
Sample uptake rate/μL min ⁻¹	40
Acetic acid concentration, % v/v	20
Primary wavelength/nm	253.7, 184.9
Irradiation time/s	~5
<i>Vis photo-assisted vapor generation with halogen lamp (SYSTEM B)</i>	
Power of halogen lamp/W	20
Solutions uptake rate/μL min ⁻¹	40
Acetic acid concentration, % v/v	20
Spectra range/nm	480 – 3400
Irradiation time/s	~5
<i>Vis photo-assisted vapor generation with LED source (SYSTEM C)</i>	
Power of LED lamp/W	3
Solutions uptake rate/μL min ⁻¹	40
Acetic acid concentration, % v/v	20
Spectra range/nm	490 – 950
Irradiation time/s	~5

materials.

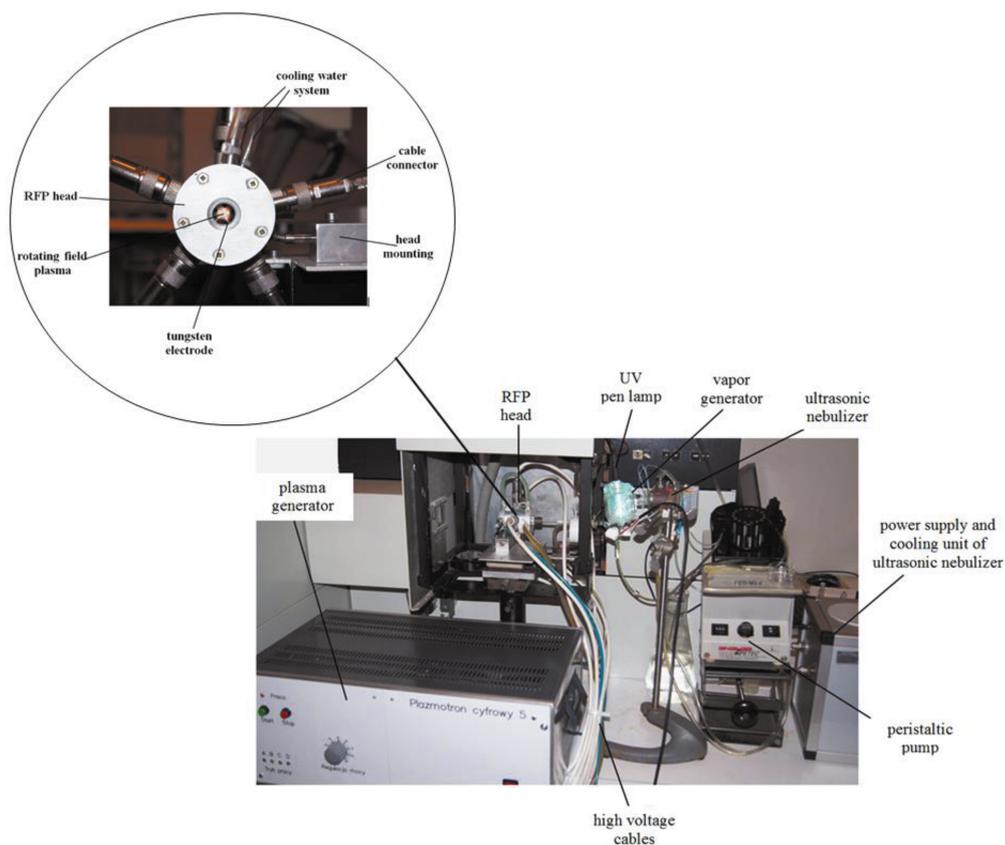
Experimental

RFP-OES Instrumentation and operating conditions

A Carl Zeiss Echelle spectrometer (Model PLASMAQUANT 100, Jena, Germany) using fiber-optic light guides, photomultiplier tubes (PMTs) and the five phase digitally controlled rotating field plasma (RFP) assembly was used. The plasma was viewed axially with the axis of the plasma perpendicular to the plane of the entrance slit. The water cooled cylindrically-shaped plasma head was equipped with five 1.6 mm diameter tungsten rod electrodes, mounted in symmetrically placed connectors. The device was installed on a specially designed three dimensional (*x* – *y* – *z*) adjustable stage, which permitted horizontal, axial and vertical positioning with an accuracy of ±0.5 mm for precise alignment of the optical discharge area, formed between electrodes, for maximum excitation. The generator ensuring rotation frequency in the range of 4 – 50 kHz and a maximum power of 250 W, was connected by means of five flexible cables to the cylindrical head. For introducing mercury vapors into the plasma, a quartz tube of 3.0 mm i.d. was inserted to the head and placed 5 mm in front of the discharge area.

The RFP-OES operating conditions, including the optimized ones that were used for the analysis of certified reference materials, are summarized in Tables 1 and 2. The emission mercury line was pre-selected by the producer of the polychromator. A schematic diagram of the entire experimental set-up (*i.e.*, sample introduction system/RFP-OES) is shown in Fig. 1.

(A)



(B)

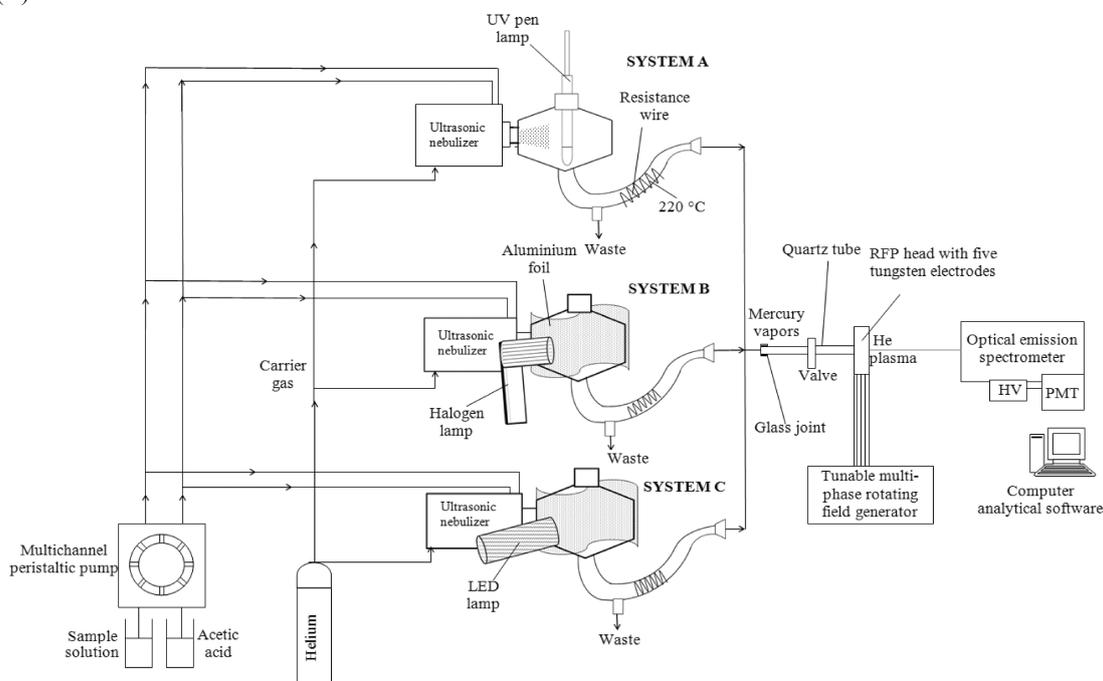


Fig. 1 Schematic view of online USN-UV/Vis-CVG-RFP-OES systems (not to scale). (A) Overview photograph of on-line USN/UV-CVG-RFP-OES system. (B) Schematic diagram of trace mercury analysis systems (A, B, C).

Five-phase digitally controlled rotating field plasma generator

For plasma generation a digitally controlled rotating field poly-phase plasma (RFP) generator described by Jankowski

*et al.*¹⁷ was used. However, the following important modifications were introduced by the authors: redesigning the power supply unit and high voltage transformers as well as

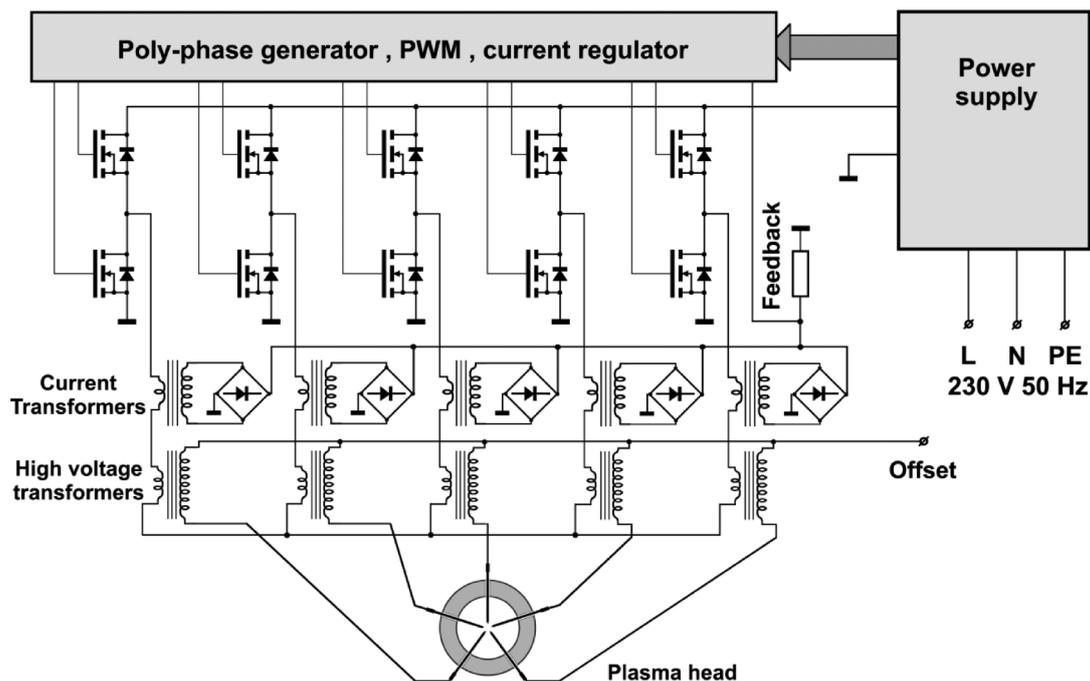


Fig. 2 Simplified electric diagram of rotating field plasma (RFP) generator.

adding an extra current feedback. The main parts of the plasma assembly are presented in Fig. 2.

The base signal is digitally produced in the generator, then it is divided into multiple 5-phase signals. Further, the pulse-width modulator (PWM) enables digital control of the forward power by changing the pulse length and the plasma excitation power. The setup consists also of a mains power supply (standard single-phase 230 V/50 Hz AC; called mains). This power supply produces a constant voltage, which, due to safety reasons, is galvanically separated (electrically isolated) from the mains and offers low output impedance and a ripple rejection.

The digital signals, galvanically coupled from the power part by the photocouplers, control 10 power transistors (see Fig. 2). The transistors work as D-class amplifiers and form a power inverter. This inverter delivers power to the plasma head through the output transformers. The output transformers provide a high output voltage to the electrodes in the plasma head as well as a galvanic isolation of the power inverter and the plasma head. This is especially important because the RFP head is water-cooled and attached directly to the grounded holder. The discharge current flow in the head induces the plasma and its shape depends on the current state of the power inverter.

Because plasma is unstable by nature, it electrically acts like a negative dynamic resistor. Therefore, the current source power supply should be used. Jankowski *et al.*¹⁷ presents the power supply as a voltage source, but in fact it is a very rough simplification. The inverter, which feeds the current to the plasma head, cannot be powered by the source with a low internal impedance. Because the voltage source has a very low internal impedance, a reducing circuit should be added to avoid damage of the inverter. A very simplified solution, which roughly approximates the current source, can be realized through a serial resistor placed between the output of the power supply to the inverter. Unfortunately, in a relatively high power system, as the device presented, the serial resistor dissipates a lot of power. The authors did not use such a passive solution,¹⁷ but proposed an active circuitry—a negative current feedback. As

an input, the feedback circuit uses a signal proportional to the output current. This feedback signal is produced by the current transformers, then it is rectified, amplified and sent to the generator circuit. In the generator it influences the pulse width of the output signal. This way the feedback stabilizes the forward power of the generator and naturally reduces the maximum output current (the voltage source may be used). Because the feedback signal has a frequency band similar to the signal produced by the generator, it can change the width of each single pulse. Therefore, the generator controls the power of each plasma pulse. In consequence, it improves the short-term stability of plasma. The short-term stability means that the power of plasma is almost not sensitive to the variations of the mains voltage. The feedback also improves long-term stability, which means that the influence of worn electrodes on plasma stability is reduced. The proposed solution with the feedback has also some drawbacks, however, namely it is more complex than the simplest solutions and it needs careful adjustment of elements and signals during the design and implementation of the system.

The plasma parameters (its shape, density and power) are affected by the modes of the field rotation. The plasma discharge occurs between two or more electrodes, where some of them act as anodes and others act as cathodes. The configuration changes from pulse to pulse depending on the phase. Although the generator offers many modes of plasma shape, the authors chose only one of them, in which the plasma discharge occurred between every other electrode. During the selected 5-phase sequence, the generator produces a rotating field in the following order: 1(C)-4(A), 2(C)-5(A), 3(C)-1(A), 4(C)-2(A), 5(C)-3(A), where the numbers indicate electrodes, and C, A is the cathode and anode, respectively (Fig. 3). A geometric arrangement of the chosen mode ensures the highest density of plasma in the center. It is very desirable during the measurements discussed. Other sequences, *e.g.* with discharges between adjacent electrodes will produce doughnut-shaped plasma¹⁷ with much less density in the center.



Fig. 3 Plasma rotation sequence on electrodes of RFP head.

However, the generator produces 5-phase rotating field plasma in a low frequency range (LF), *i.e.* 20 – 100 kHz, the 5-phase cycle results in a field rotation frequency that is 5 times lower. It means that the field rotation frequency can vary between 4 and 20 kHz. For the measurements discussed, the frequency of the base signal produced by the generator was fixed at 60 kHz (the plasma field rotation frequency equals 12 kHz). Also, the design parameters of the transformers and the current feedback were optimized just for this frequency.

Ultrasonic nebulization-ultraviolet/visible light irradiation vapor generation

Three photo-generation systems were investigated, as schematically illustrated in Fig. 1(B).

The first, photochemical mercury vapor generation was accomplished in the continuous mode using a commercial ultrasonic nebulizer (Model NOVA-DUO, Optolab, Warsaw, Poland) equipped with a water-jacketed glass cyclonic spray chamber (internal volume of 50 mL), into which a 6 W Hg UV pen lamp was placed vertically. There were two principal emission lines from the mercury lamp in the UV range, 254 and 185 nm. Sample solution and acetic acid were delivered by two separate PFA capillaries (0.4 mm orifices) positioned at an angle of 45 degrees and placed in almost direct contact with the quartz surface of the ultrasonic transducer. In this manner two independent solutions are pumped simultaneously onto the surface of a quartz piezoelectric transducer (1.65 MHz resonant frequency, with a forward power of 80 W) at a flow rate of 40 $\mu\text{L min}^{-1}$ using a Perimax12 peristaltic pump (SPETEC, Erding, Germany), where they were effectively mixed and dispersed into droplets of approximately 2.0 – 2.5 μm in mean droplet diameter (0.1 – 4.5 μm size distribution; a very fine aerosol is formed as a result of the interaction between ultrasonic waves and the liquid film).¹⁸ The ultrasonic nebulizer is directly connected to the cyclonic glass spray chamber. The transducer quartz plate and radiator were cooled with a closed circuit water cooling system; the system was used without desolvation. To prevent the analyte (aerosol) from depositing on the plasma quartz torch, the spray chamber glass outlet was electrically heated by means of a 15 cm wrapped heating wire. The cyclonic spray chamber was connected with the nebulizer body using a glass joint. A schematic of the photochemical reactor housing a 6 W Hg UV pen lamp is presented in Fig. 1(B). The liquid samples were delivered to the photoreactor by use of a peristaltic pump. The gas flow rate was controlled by means of a mass flow controller (DHN, Warsaw, Poland) with a pressure regulator. Helium was used as the nebulizing-carrier gas and plasma gas. The flow rate of aerosol was maintained with an external mass flow controller.

Figure 1(B) illustrates the second arrangement in which aerosols generated in a glass spray chamber by ultrasonic nebulizer were irradiated using a 20 W (40 mW cm^{-2}) halogen lamp (Biopton, Zepter, Wollerau, Switzerland) emitting Vis/IR

irradiation. One side of the spray chamber was loosely enveloped with aluminum foil to reflect radiation from the lamp so as to increase the efficiency of irradiation. Similarly, in the third configuration (Fig. 1(B)) a 3 W Vis light LED source (Type P3830, Emos, Bielsko-Biala, Poland) was mounted nearby the glass spray chamber.

Reagents

Pure and compressed helium (N-50 purity, 99.999%) obtained from BOC GAZY (Poznań, Poland) was used for nebulizing and as a plasma gas. Acetic acid 20% (v/v) (Merck, Darmstadt, Germany) was applied as low molecular weight organic precursor to obtain the photochemical vapor generation. Test solutions of inorganic mercury were prepared by serial dilution of a 1000 mg L^{-1} stock (Titrisol grade) sourced from Merck (Darmstadt, Germany). Working standards were prepared daily to prevent any possible concentration changes, by diluting appropriate aliquots of the stock solution in deionized distilled water or in 20% v/v acetic acid and kept in the dark until used. Water was initially deionized (DEMIWA 5 ROSA, Watek, Czech Republic) and then doubly distilled in a quartz apparatus (Heraeus Bi18, Hanau, Germany).

Reference materials

Applicability of the method described in this work was assessed using three reference materials chosen to represent solid sample matrices: NRCC DOLT-2 (Dogfish Liver) and NRCC PACS-1 (Marine Sediment) supplied by the National Research Council of Canada (NRCC, Ottawa, Canada) and NIST 2710 (Montana Soil) supplied by NIST (Gaithersburg, MD). Certified reference values for mercury are available for assessment of the quality assurance and method validation. These materials were used as bottled, without further grinding and sieving.

Procedure for ultrasound-assisted solubilization of biotissue

Approximately 250 – 300 mg of powdered biological tissue reference material DOLT-2 were put into a 25-mL pre-cleaned polypropylene vessel into which 20% v/v acetic acid was added. The vessel was subjected to probe sonication (Bandelin, model SONOPULS HD 70, Berlin, Germany) for 3 min at 60 W with a 3-mm diameter sonotrode immersed into the sample solution. After two hours the sample was transferred quantitatively to a volumetric flask and filled up with water to the final volume of 10 mL. This solution can be measured directly or after dilution, depending on the concentration level of the mercury. A corresponding blank was also prepared according to the above ultrasound-assisted solubilization procedure. Calibration solutions were prepared in deionized distilled water.

Microwave digestion system

A laboratory-built prototype of a high pressure temperature focused microwave heating digestion system, equipped with

closed TFM-PTFM (Hostafion TFM is a chemically modified PTFE) vessel (30 mL internal volume) based on a design outlined in detail by Matusiewicz,¹⁹ was employed for wet-pressure sample (NRCC PACS-1, DOLT-2 and NIST 2710) digestion.

Microwave-assisted sample digestion at high pressure in TFM-PTFE vessels for inorganic reference materials

Preparation of all standards and digestion of all samples were conducted under typical laboratory conditions. The microwave-assisted pressurized digestion technique used for biological and environmental samples has been described previously.¹⁹

Approximately 250 – 300 mg of powdered inorganic reference materials (NRCC PACS-1 and NIST 2710) were first moistened by 0.5 mL of 30% H₂O₂; then 2 mL of concentrated HNO₃ and 2 mL of 40% HF were used. The samples were heated for 15 min at 150 W. The digested solutions were transferred into 10 mL volumetric calibrated flasks and diluted up to the mark with distilled water. Before further analysis they were appropriately diluted depending upon the concentration level of mercury. In all cases, a corresponding blank was also prepared according to the above microwave-assisted dissolution procedures.

RFP-OES analysis

The digitally controlled plasma was ignited spontaneously when the generator power was set approximately at 100 W and then was allowed to warm up for a period of about 15 min prior to analysis. The aerosol of the sample solution and 20% acetic acid was irradiated with the UV or the Vis source. When generation was completed, the mercury vapors released were immediately carried out by the helium carrier gas through the cyclonic spray chamber and into the RFP for excitation in the helium plasma gas. The whole procedure would take about 1 min. Net analyte emissions were recorded and calculated by taking the simultaneous difference of measured emission intensities on the top of the peak and background near the peak. Instrumental characteristics and operating parameters with the use of the experimental USN-UV/Vis-CVG-RFP-OES systems are listed in Tables 1 and 2. Analytical blanks were also carried through the entire procedure outlined above to correct for possible contaminants in the reagents used for sample preparation. Quantification of mercury was made from external linear calibration curves. All limits of detection (LOD) given by software were calculated for raw, unsmoothed data based on a 3 σ criterion of the background (blank) counts. The LOD, corresponding to a measurement level 3 σ above the mean blank intensity, was obtained by using procedural blank solutions.

Results and Discussion

The effect of operating parameters on digitally controlled plasma

Although many of the signal parameters that control the plasma in an RFP-OES system can be changed easily by means of digital signal processing (DSP), the possibilities of these changes also diminish due to some other elements used in the assembly.

The most important parameters to optimize are from the high voltage transformers. The voltage on the electrodes in the plasma head must be high enough to introduce the electric discharge between the electrodes. The bigger the electrode spacing is, the higher the so called open circuit voltage (OCV) must be. The minimum OCV depends not only on the distance between electrodes, but also on the gas flow rate, so to achieve

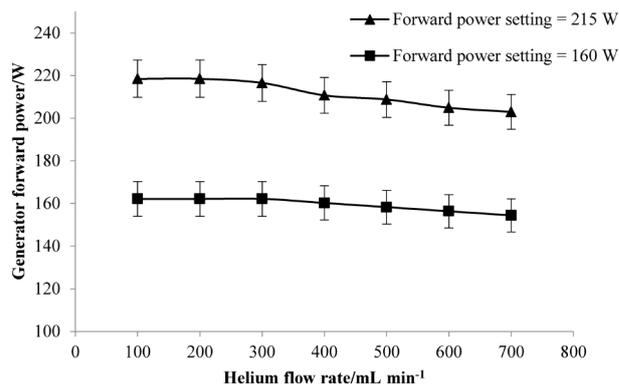


Fig. 4 Generator forward power as a function of helium flow rate.

reasonable plasma parameters it cannot be too low. In direct power inverter solutions (without output transformers) the electrodes are driven directly by transistors.¹⁷ Typical transistors, available on the market, offer the maximum collector-emitter (or drain-source) voltage equal to approx. 1 kV. Due to required margin of safety for the switching transistors, the OCV should be lower than 1 kV. In consequence, it hardly reduces the spacing between electrodes and hampers the self-start of the plasma. In the setup presented, special high voltage output transformers designed by the authors were used. The secondary winding of the transformer designed works with OCV equal to about 4 kV.

Power is another important parameter for measuring plasma. To reach proper conditions for the experiment, the power of plasma should be tuned. In the solution presented, the forward power is regulated by the PWM (pulse width modulator). In theory, the pulse width can vary between 0 and 100%, where 0% means a signal cancellation and 100% means the fully saturated signal, but in practice the modulation cannot be so deep. The values near zero produce very short peaks which destabilize the operation of the inverter or may even result in a short circuit of the power supply. On the other hand, pulses that are too long saturate the transformer core, resulting in lower total energy efficiency. The carefully prepared design followed by the particular circuit tuning allow to avoid such hazards. In the setup described, the PWM is limited to the range between 10 and 90% and is additionally affected by the current feedback.

As mentioned above, the forward power of the plasma generator can be controlled by modifying the base signal frequency, pulse width and sequence mode, but it is also affected by *e.g.*, the mains voltage and gas flow rate. In the setup presented the base signal frequency and the sequence mode were fixed (see Table 1), while the generator forward power, which excites the plasma was controlled by the width of the output signal pulses (PWM). The power can be set by the operator with the power knob. In fact, the real power may vary even if it is fixed by the operator. There are two main sources of these variations: fluctuations of the mains voltage and the gas flow rate. While the impact of the voltage supplied on the power is obvious, the second source is indirect. As it was mentioned above, the plasma acts electrically as a varying resistor. The resistance match between the power generator and the plasma head is worse in the case of higher gas flow rates. This results in a power drop. Fortunately, these problems are significantly reduced by the use of the current feedback. Figure 4 presents the impact of the gas flow rate for two example power settings, while the gas flow rate changes from

Table 3 Optimum operating conditions for USN-UV/Vis-CVG-RFP-OES measurement^a of mercury vapor in soluble materials obtained by simplex and univariate methods

Parameter (variable)	Boundary limits of parameters, range				Univariate method				Simplex method			
	USN	SYSTEM A	SYSTEM B	SYSTEM C	USN	SYSTEM A	SYSTEM B	SYSTEM C	USN	SYSTEM A	SYSTEM B	SYSTEM C
Forward power/W	100 – 220	100 – 220	100 – 220	100 – 220	220	200	200	200	195	200	200	195
Plasma helium flow rate/mL min ⁻¹	100 – 600	100 – 600	100 – 600	100 – 600	200	200	200	200	205	206	212	195
Sample liquid uptake rate (pumped)/ μ L min ⁻¹	5 – 100	5 – 100	5 – 100	5 – 100	45	40	40	40	45	38	42	38

a. Response, peak height of the mercury emission intensity.

100 to 700 mL min⁻¹. It should be noted that even higher gas flow rates do not extinguish the plasma significantly. In consequence, in typical measurements, with power at less than 200 W, the effect can be neglected. The generator guarantees stability of the plasma discharge almost regardless of the settings of the sample preparation.

USN-UV/Vis-CVG design

A group of UV/Vis reactors (three photogeneration systems) was examined to elucidate an optimal experimental approach. The new tandem system of combined ultrasonic micro-flow nebulizer and UV/Vis irradiation systems connected in series was chosen and used to generate the vapors of mercury. Their structures were shown in Fig. 1. In these systems (USN-UV/Vis-CVG) the aerosol was formed first and then exposed to the UV or Vis field. Photoreduction took place in a flow-through system, with a pen lamp immersed into the analyte solutions (aerosols) and halogen lamp or LED lamp mounted nearby the glass spray chamber for aerosols irradiation. System A (USN-UV-CVG) was the optimum design among the three systems examined and was chosen as the practical design for this work.

Optimization of operating parameters

In order to test the applicability of the USN-UV/Vis-CVG systems for vapor generation to RFP-OES, an optimization of Hg emission signal intensities as a function of the different parameters was carried out.

Optimization of all operating conditions simultaneously by simplex procedures was undertaken in these investigations for mercury determination.

Two different types of experimental variables affect the method. These are as follows: first, variables controlling the emission response in the five phase digitally controlled rotating field plasma, that is, the forward power of the generator; and second, variables such as the helium carrier flow and sample uptake rate that regulate transport. The maximum and minimum levels of the variables to be investigated are shown in Table 3. In addition, Table 4 lists the optimum values that the experiments carried out using the simplex method indicated for mercury of the three factors studied.

In this work, the stable He plasma could be maintained at a level of greater than 130 W (Fig. 5(a)) forward power. Between 130 and 190 W, an increase of the intensity of analytical signals was observed. The intensities of mercury signals leveled off with power approaching 190 W. Therefore, an optimized power of 200 W was selected as an acceptable value and a practical working range.

Table 4 Optimum operating conditions for the mercury determination by USN-UV/Vis-CVG-RFP-OES systems

Parameter	USN	USN-UV/Vis-CVG system		
		SYSTEM A	SYSTEM B	SYSTEM C
Applied power/W	200	200	200	200
Helium flow rate/mL min ⁻¹	200	200	200	200
Sample liquid uptake rate (pumped)/ μ L min ⁻¹	45	40	40	40

Because the aerosol carrier gas flow rate affects analyte transport efficiency and residence time in the plasma, further optimization of this parameter was guaranteed to achieve both plasma robustness and efficient analyte transport into the RFP. To optimize the carrier helium gas flow through the USN-UV/Vis system for mercury determination, the optimum flow was estimated in the total range of 100 – 250 mL min⁻¹ for RFP-OES (Fig. 5(b)). In general, it was observed that when the flow rate ranged between 150 – 250 mL min⁻¹, the emission intensities reached maximum at 200 mL min⁻¹ for the USN-UV/Vis-CVG system, and with a further increase of the flow rate above this value, the emission intensities decreased. Therefore, in this study, a 200 mL min⁻¹ carrier helium flow rate was chosen for USN-UV/Vis-CVG-RFP-OES system.

Acetic acid was used as the reductant and functioned as the acidic medium at the same time, and this led to the simplest possible photo-induced CVG system, CH₃COOH-Hg²⁺. The efficiency of the photo-induced CVG was found to be acetic concentration-dependent, both with the UV or Vis irradiation.

Acetic acid concentration for mercury determinations was optimized in the range of 10 – 50% (v/v) (Fig. 5(c)). Intensities for mercury decreased with an increasing concentration of acetic acid over 20% (v/v). Therefore, in this study, a 20% (v/v) acetic acid concentration was adopted.

The sample uptake rate critically influences mercury vapor generation and plasma stability. To optimize the sample flow rate for mercury determination, first the optimum flow rate for mercury was estimated within the range of 10 – 50 μ L min⁻¹ (Fig. 5(d)). It was observed that when the flow rate was low (10 – 40 μ L min⁻¹), the emission intensities increased with the flow rate; when the flow rate went up to around 40 μ L min⁻¹, the emission intensities reached maximum. However, with a further increase of the flow rate (above 40 μ L min⁻¹), the emission intensities would not increase further and began to

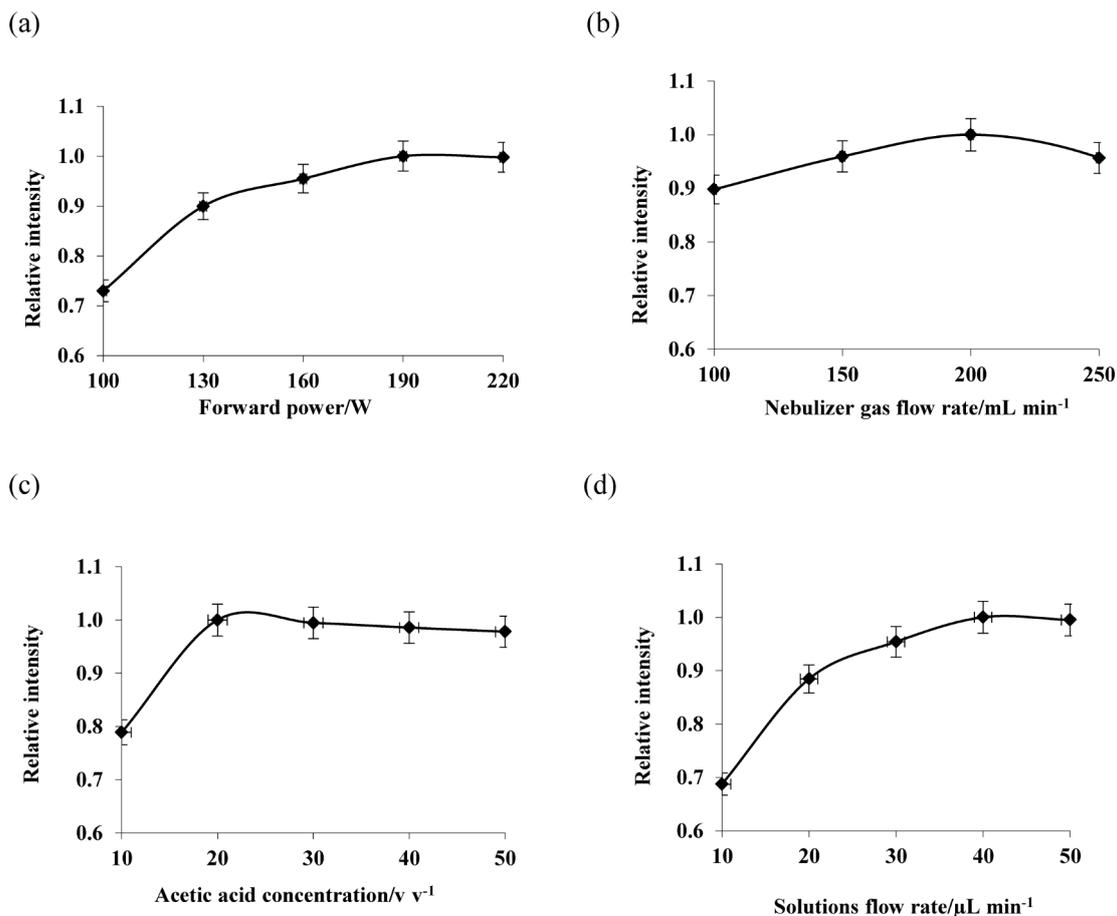


Fig. 5 Effect of the variables on the mercury normalized emission intensity for USN-UV/CVG-RFP-OES system. Influence of (a) RFP forward power; (b) nebulizer helium gas flow rate; (c) acetic acid concentration; (d) solution flow rate on the mercury analytical emission signal intensity.

decrease for mercury. Therefore, in this study, a 40 $\mu\text{L min}^{-1}$ sample flow rate was chosen.

The wash-out time required for the net analyte signal to decay to 1% of its steady-state signal value was 3 min using acetic acid.

Analytical figures of merit

Under optimized experimental conditions, the analytical performance of the proposed method for the determination of total mercury (Hg^{2+}) was investigated. The LOD calculated using the IUPAC recommendation (based on a $3\sigma_{\text{blank}}$ criterion), determined by 10 repetitive measurements of the blank involving the entire process and obtained by use of the compromise operating conditions is summarized in Table 5 and is based on the raw, unsmoothed data. The LODs (15 to 17 ng mL^{-1}) for mercury using USN/Vis-RFP-OES (System B,C) are slightly better and evidently better (4.1 ng mL^{-1}) for systems based on UV photochemical vapor generation (System A) than that achieved with solution ultrasonic nebulization (USN). The comparison of the results obtained in this work with the works found in the literature shows that the detection limit of USN/UV-CVG-RFP-OES for Hg (4.1 ng mL^{-1}) is slightly better than the results obtained by the digitally controlled rotating field He plasma—OES by Jankowski *et al.* (5.3 ng mL^{-1})¹⁷ and by 3-phase MIP-OES by Jankowski *et al.* (9 ng mL^{-1}).¹⁵

The precision expressed as relative standard deviation (RSD, $n = 10$) with USN-UV/Vis-CVG-RFP-OES is given in Table 5

Table 5 Analytical figures of merit

Parameter	USN	SYSTEM A	SYSTEM B	SYSTEM C
Limit of detection (3σ)/ ng mL^{-1}	23	4.1	17	15
Limit of detection ^a (3σ)/ $\mu\text{g g}^{-1}$	0.76	0.14	0.57	0.50
Absolute detection limit ^b / ng	0.92	0.16	0.68	0.60
Precision, % RSD	5	5	7	4

a. For sample weights of 300 mg, b. Sample solution flow rate of 40 $\mu\text{L min}^{-1}$.

for solution of Hg^{2+} in 20% acetic acid. The precision of replicate determinations was calculated from the RSD (%) of the mean of 10 replicate measurements of element standard using a mass 50-fold above the LOD. The average precision for mercury was in the range of approximately 5% (evaluated as peak height).

Validation and analytical application to reference materials

To evaluate the accuracy and precision of the sample introduction system tested on the vapor forming mercury, three certified reference materials were chosen because they were the

Table 6 Analysis of certified reference materials (concentrations in $\mu\text{g g}^{-1} \pm \text{SD}$ of three parallel determinations) for mercury determination

Photogeneration system	Dogfish Liver NRCC DOLT-2		Marine Sediment NRCC PACS-1		Montana soil NIST 2710	
	Found value/ $\mu\text{g g}^{-1}$	Certified value/ $\mu\text{g g}^{-1}$	Found value/ $\mu\text{g g}^{-1}$	Certified value/ $\mu\text{g g}^{-1}$	Found value/ $\mu\text{g g}^{-1}$	Certified value/ $\mu\text{g g}^{-1}$
USN	2.09 ± 0.12	1.99 ± 0.10	4.50 ± 0.23	4.57 ± 0.16	6.35 ± 0.32	6.25 ± 0.19
SYSTEM A	2.03 ± 0.10		4.61 ± 0.28		6.31 ± 0.32	
SYSTEM B	2.03 ± 0.14		4.65 ± 0.36		6.39 ± 0.49	
SYSTEM C	1.97 ± 0.08		4.55 ± 0.20		6.28 ± 0.25	

closest in their nature to real biological and environmental samples. The results obtained for the analysis of reference materials by USN-UV/Vis-CVG-RFP-OES method using the external calibration technique, are summarized in Table 6. The results obtained by the external calibration standards prepared in aqueous solutions agree with certified values for three reference materials, indicating that calibration against an aqueous solution could produce accurate results. All experimental concentrations agreed fairly well with the certified interval element values (according to the Student's *t*-test). The average precision for mercury of replicate determinations was in the range of approximately 5% RSD. Therefore, the proposed method was found to be accurate and reliable and was suitable for routine testing.

Conclusions

A new, power-efficient technique based on USN-UV/Vis-CVG with RFP-OES detection has been developed for the determination of mercury. The experiments performed proved that UV-Vis cold Hg vapor generation can fully substitute conventional methods of photochemical and chemical mercury vapor generation ($\text{NaBH}_4/\text{KBH}_4$ and/or SnCl_2), according to "green analytical chemistry" demands. Photolysis based on UV and Vis sources of acetic acid gives rise to radicals capable of reducing Hg^{2+} .

The 5-phase rotating field helium plasma generator offers high possibility of changes of many parameters, such as mode of the plasma sequence generation, plasma excitation power, field rotation and, due to the modifications presented, improves the quality of measurements. However, the 5-phase rotating field helium plasma is not resistant to high solvent loading because of low power levels, therefore, it is not suitable for standard nebulization with flow rates in the range of 1 – 2 mL min^{-1} . The improvement of the analyte(s) emission intensity resulting in a lowering of detection limits could be expected for higher power levels.

The continuous development of electronics, both digital and power analog components, will broaden the horizons of measurements and analytics that use digitally controlled plasmas.

Acknowledgements

The authors gratefully acknowledge financial support from the

National Science Center (NCN), Poland (Grant No. UMO-2012/06/A/ST4/00382). The assistance and cooperation of ERTEC, Wrocław, Poland in obtaining the rotating field plasma head and poly-phase plasma generator is also acknowledged.

References

- USEPA 823-R-10-001, U.S. Environmental Protection Agency, Office of Water, Washington, D.C., **2010**.
- Y. Gao, Z. Shi, Z. Long, P. Wu, C. Zheng, and X. Hou, *Microchem. J.*, **2012**, *103*, 1.
- H. Matusiewicz and R. E. Sturgeon, *Appl. Spectrosc. Rev.*, **2012**, *47*, 41.
- R. E. Sturgeon and Z. Mester, *Appl. Spectrosc.*, **2002**, *56*, 202A.
- L. Gámiz-Gracia and M. D. L. de Castro, *J. Anal. At. Spectrom.*, **1999**, *14*, 1615.
- Y. He, X. Hou, C. Zheng, and R. E. Sturgeon, *Anal. Bioanal. Chem.*, **2007**, *388*, 769.
- C. Bendicho, F. Pena, M. Costas, S. Gil, and I. Lavilla, *TrAC, Trends Anal. Chem.*, **2010**, *29*, 681.
- P. Wu, L. He, C. Zheng, X. Hou, and R. E. Sturgeon, *J. Anal. At. Spectrom.*, **2010**, *25*, 1217.
- Y. Yin, J. Liu, and G. Jiang, *TrAC, Trends Anal. Chem.*, **2011**, *30*, 1672.
- G. Woldemichael, T. Tulu, and G.-U. Flechsig, *Int. J. Electrochem.*, **2011**, Article ID 481370.
- G. Woldemichael, T. Tulu, and G.-U. Flechsig, *Microchim. Acta*, **2012**, *179*, 99.
- K. J. Jankowski and E. Reszke, "Microwave Induced Plasma Analytical Spectrometry, RSC Analytical Spectroscopy Monographs No. 12", **2011**, Royal Society of Chemistry.
- K. J. Jankowski and E. Reszke, *J. Anal. At. Spectrom.*, **2013**, *28*, 1196.
- M. Ślachciński, *Appl. Spectrosc. Rev.*, **2014**, *49*, 271.
- K. J. Jankowski, A. P. Ramsza, E. Reszke, and M. Strzelec, *J. Anal. At. Spectrom.*, **2010**, *25*, 44.
- K. J. Jankowski, A. P. Ramsza, and E. Reszke, *Spectrochim. Acta, Part B*, **2011**, *66*, 500.
- K. J. Jankowski, A. P. Ramsza, E. Reszke, and A. Tyburska, *J. Anal. At. Spectrom.*, **2012**, *27*, 1287.
- Q. Jin, C. Zhu, K. Brushwyler, and G. M. Hieftje, *Appl. Spectrosc.*, **1990**, *44*, 183.
- H. Matusiewicz, *Anal. Chem.*, **1994**, *66*, 751.