Talanta 147 (2016) 28–34

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

The construction and testing of the portable Hg^{2+} ultrasonic calibrator for the control of mercury speciation systems

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ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form
5 September 2015
Accepted 7 September 2015
Available online 9 September 2015

Keywords:
$HgCl_2$
Ultrasonic calibrator
Mercury speciation
Flue gases

ABSTRACT

During fuel combustion mercury, as Hg^0 and Hg^{2+} forms, is emitted to the atmosphere. Effective reduction of mercury emission requires applying speciation systems for emission control and research. An important part of all mercury determination and speciation systems are the calibrators. Calibrators are responsible for the accuracy of mercury determination and, in consequence, the effective reduction of mercury emission. The aim of the work was to construct a portable $HgCl_2$ calibrator. The purpose of the device was the control of mercury speciation systems for continuous measurements and study of $HgCl_2$ sorption. As a result of previously conducted research, the portable Hg^{2+} ultrasonic calibrator was designed, constructed and tested. The ultrasonic calibrator generates a stable stream of $HgCl_2$ (RSD=2.8% for $C_{Hg}=28\ \mu g/m^3$). The correlation between theoretical and reading concentration of $HgCl_2$ was $R^2=0.9983$. The average recovery of $HgCl_2$ was 95%. The advantages of the ultrasonic Hg^{2+} calibrator are: high accuracy and selectivity, low pressure of $HgCl_2$ stream and very low cost of production. The calibrator was successfully tested, both in the laboratory and in the power plant, during a preliminary study on $HgCl_2$ sorption on a fly ash filter.

1. Introduction

The anthropogenic emission of mercury is estimated at 1960 t per year [1]. Industrial sources are responsible for more than 85% of mercury emitted to the atmosphere [2,3] and [4]. Mercury can enter the air in three main forms as Hg^0, Hg^{2+} and Hg_p (Particle Bound Mercury) [5] and [6]. These forms have different properties. Hg^0 is a global pollutant, because it can be transported for long distances. Hg^{2+} is a more local contaminant. It is water-soluble and may enter the water reservoir with precipitation. In the bottom sediments Hg^{2+} could be transformed into the highly toxic methylmercury and after biomagnification may reach a level hazardous to living species. MeHg can return to the atmosphere as a part of mercury reemission [7–9] and [10].

Due to the high toxicity of mercury, its sources have systematically been eliminated for many years [11,12] and [13]. The Minamata Convention signed by 102 countries in 2013 is the next global-scale stage of mercury emission reduction. Studies on the removal of mercury from processing gases and anthropogenic waste are performed in order to effectively eliminate mercury emissions [14,15] and [16]. One of the growing sectors of mercury analysis is its speciation. Knowledge of the forms of mercury released into the environment is essential for effective emission reduction [17–19] and [20]. The processes of fossil fuel combustion are responsible for the majority of mercury emissions in many countries [21–25] and [26]. Combustion control and mercury oxidation in flue gases combined with Hg speciation are effective tools for mercury emission reduction [27–29] and [30]. Mercury speciation systems for continuous measurements require mercury calibrators to ensure the quality of the results; Hg^0 calibrators based on mercury vapor pressure that change with temperature. In the case of ionic mercury calibrators two main types are used: evaporators and converters. Evaporator calibrators use $HgCl_2$ solutions as a source of ionic mercury. Typically the high pressure inert gas is used for the process of nebulisation. Conversion Hg^{2+} calibrators oxidize elemental mercury to get ionic mercury. There are only a few ionic mercury calibrators commercially available: Tekran 3315-Ionic Mercury Calibration Unit (Tekran® Instruments Corporation), VICI 500 Dynacalibrator (VICI Metronics), HovaCAL-Calibration Gas Generator (IAS GmbH). In literature on the subject information on the construction of ionic mercury calibrators is very rare [31].

Ultrasounds are used in analytical chemistry for sample preparation, mainly in extraction processes [32–35] and [36]. Another ultrasound application in chemistry are sample delivery systems; for example, in ultrasonic nebulizers for ICP [37–39] and [40].

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http://dx.doi.org/10.1016/j.talanta.2015.09.019
0039-9140/

Ultrasonic nebulizers are also used in medicine (drug administration) [41] and [42] and as household appliances (humidifier devices) [43].

The purpose of this paper is to present the construction and test of a portable, inexpensive, ionic mercury ultrasonic calibrator. The calibrator was designed for the control of mercury determination and speciation systems for continuous measurements and for use in any study requiring a stable and low-pressure stream of ionic mercury vapors.

2. Materials and methods

2.1. Apparatus

The ionic mercury ultrasonic calibrator (IMUC) uses ultrasound to nebulize the standard $HgCl_2$ solution and then transform the solution fog into steam in 453 K. The IMUC was designed for calibration and control of continuous measurement mercury speciation systems. It could also be used in any experiment that needs a constant stream of ionic mercury (e.g. fly ash sorption or mercury sorbent study), especially when a low-pressure ionic mercury stream is required.

The main part of the IMUC (Fig. 1) is commercially available, a modified 12–30 W ultrasonic humidifier (1). Inside the humidifier bathtub, the fog chamber is installed (2). A thin-wall, 100 ml PET bottle was used as a fog chamber. The bottle material and its weight are crucial, because the bottle has to transmit ultrasonic vibration. In the upper part of the bottle the connector (3) for a 3.2 mm Tygon tube is installed. The Tygon tube connects the fog chamber and the peristaltic pump (4). In the final version of the calibrator the PLP 66 pump (Behr, Germany) was applied. The pump provides a constant flow of air (or another gas). The pump flow rate may be changed in range from 50 to 340 cm^3/min. The carrier gas is purified by a carbon filter (5) mounted at the pump inlet. The outlet of the fog chamber is coupled to an L-shaped PTFE evaporation chamber (6). The shape of the evaporation chamber is very important. The proper shape allows for the removal of big drops and provides stable Hg^{2+} generation. The output of the evaporation chamber is connected to a 1 m long PTFE transfer line (7). The transfer line is a 6 mm PTFE tube covered with heating and insulation tapes. The transfer line and the top part of the evaporation chamber (smaller diameter tubing) is heated to 453 K. As the ultrasonic generator heats the water in the bathtub, the temperature of the fog chamber is stabilized with a temperature controller (8) connected to a temperature sensor (9) and a fan (10). To keep the calibrator level, especially in its industrial application, the device is equipped with adjustable legs (11) and a spirit level (12). All parts of the device are mounted in a portable container.

The use of ultrasound in the ionic mercury calibrator enables the device to separate the $HgCl_2$ solution nebulization and ionic mercury transfer functions. It is especially important in the case of detectors that are sensitive to changes in pressure levels (like the EMP-2 mercury detector). The ionic mercury ultrasonic calibrator presented in this paper is an inexpensive device that is simple to produce. The entire cost of the IMUC was about $1200. For comparison, the cost of the Tekran 3315 Ionic Mercury Calibrator Unit is about $39,500.

For the laboratory test of the IMUC the EMP-2 WLE-8 mercury speciation set (Nippon Instruments Corporation – NIC) was applied. Briefly, the set consists of two EMP-2 (CV AAS) mercury analysers and two scrubber units. Each scrubber unit consists of three scrubbers. The first scrubber in the unit is filled with 10% $SnCl_2$ (Hg^{2+} reduction) or 10% KCl (Hg^{2+} removal/sorption), the second with a 10% KOH solution (acid gases removal/sorption). The last scrubber reduces the humidity to protect the EMP-2 detectors. The scrubbers are cooled down to about 278 K. The EMP-2 detector is a pressure-sensitive device. During the measurements in over or under pressure the procedure of result correction must be applied. The procedure is described in Section 3.2.6. The detection limit of the EMP-2 is 0.1 $\mu g/m^3$. In the stable measurement mode, the detector performs one measurement per second.

For the industrial test of the ionic mercury ultrasonic calibrator the NIC speciation set was additionally equipped with heated: probe (ZAM Kety, Poland), ash filter (AGH UST, Poland), transfer line (JCT, Austria), and the tee connector (AGH UST, Poland).

For the total Hg determination in the $HgCl_2$ standard solution and fly ash samples the MA-3000 (NIC) mercury analyzer was used.

2.2. Reagents

All reagents and standards were of an analytical grade or higher. Deionised water was purified by using the HLP5 (Hydrolab) system. Working $HgCl_2$ solutions were prepared by diluting a certified standard solution (100.12 ± 0.27 mg kg^{-1}, Inorganic Ventures). $SnCl_2$ (Avantor Performance Materials Poland S.A.) powder was used to prepare a 10% $SnCl_2$ solution for Hg^{2+} reduction. KCl powder (Chempur S.A.) was used to prepare a 10% KCl solution for Hg^{2+} absorption. Concentrated 95–98% H_2SO_4 (Aldrich) was used to acidify the $SnCl_2$ solution. Concentrated 70% HCl (J.T.Baker) was used to acidify the KCl solution. The Hg^0 standard gas was prepared in 10 dm^3 Tedlar bags (Supelco) with the use of the MB-1 gas box (NIC) and the PS-4 sampler unit (NIC).

3. Results and discussion

Several versions of the ionic mercury calibrator were designed, constructed and tested. The versions of ultrasonic calibrators

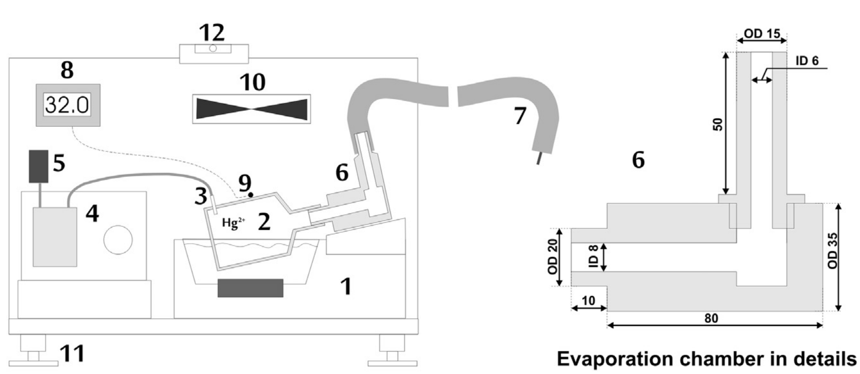

Fig. 1. Ionic mercury ultrasonic calibrator and evaporation chamber scheme.