The Utilization of Nitrogen Gas as a Carrier Gas in the Determination of Hg Ions Using Cold Vapor-Atomic Absorption Spectrophotometer (CV-AAS)

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Received March 17, 2017; Accepted December 14, 2017

ABSTRACT

The research about utilization of nitrogen gas as a carrier gas in the determination of Hg ions by using Cold Vapor-Atomic Absorption Spectrophotometer (CV-AAS) method has been conducted. To optimize the measurement results, several parameters that affect hydride generator have been studied. Some specified important parameters are $SnCl_2$ concentration as reductant, acid concentration, and the analytical performance such as repeatability and reproducibility (% RSD), linearity (r), limits of detection (LOD) and limits of quantitation (LOQ), and accuracy have been studied. The results of the research showed that the nitrogen gas can be used instead of argon gas as a carrier gas. It was shown by the repeatability values as % RSD < 2/3 CV Horwitz values, the LOD was 0.0338 µg/L and the LOQ was 0.0838 µg/L. The accuracy of this method was well shown by a recovery percentage of 102.24%. Based on the result of this research, the nitrogen gas can be used as a carrier gas for the determination of Hg ions by using the CV-AAS method with valid results.

Keywords: *Hg; carrier gas; nitrogen; CV-AAS*

ABSTRAK

Penelitian tentang pemanfaatan gas nitrogen sebagai gas pembawa dalam penentuan ion Hg dengan menggunakan metode Bejana Uap Dingin-Spektrofotometer Serapan atom (CV-AAS) telah dilakukan. Untuk mengoptimalkan hasil pengukuran, beberapa parameter yang berpengaruh dalam pembangkit hidrida telah dipelajari. Beberapa parameter penting yang ditentukan adalah konsentrasi $SnCl_2$ sebagai reduktor, konsentrasi asam, dan kinerja analitik yang meliputi penentuan kedapatulangan dan kebolehulangan (% RSD), linearitas (r), limit deteksi (LOD) dan limit kuantitasi (LOQ), dan akurasi. Hasil penelitian menunjukkan gas nitrogen dapat digunakan sebagai pengganti gas argon sebagai gas pembawa, ditunjukkan dari nilai kedapatulangan sebagai % RSD < 2/3 nilai KV Horwitz, LOD sebesar 0,0338 mg/L dan LOQ adalah 0,0838 mg/L. Ketepatan metode ini sangat baik yang ditunjukkan dengan persentase perolehan kembali 102,24%. Berdasarkan hasil penelitian ini, gas nitrogen dapat digunakan sebagai gas pembawa untuk penentuan ion Hg dengan menggunakan metode CV-AAS dengan hasil yang valid.

Kata Kunci: *Hg; gas pembawa; nitrogen; CV-AAS*

INTRODUCTION

Mercury (Hg) is a toxic element that can be found in different chemical forms at trace levels and it is very reactive in the environment. Hg is obtained in nature and distributed throughout the environment in the inorganic and organic forms (for example methylmercury) of the element [1]. Hg can be found mostly in the atmosphere, water, soil, sediments, plants, pharmaceuticals, industrial waste, mining materials and animals. The main indirect source of human contamination of Hg is through the consumption of fish products [2-3]. Undoubtedly, the natural occurrence of Hg can be found in crude oil and its presence in fuels [4]. Thus, the need for the development and validation of analytical methodologies for the determination and control of this toxic metal in samples is evident.

Several methods for the determination of Hg have been reported in the literature, such as potentiometric titration using iodide ion-selective electrodes and anodic stripping voltammetry [5], and some spectrometric techniques, such as cold vapor atomic absorption spectrometry (CV-AAS) [6-7], electrothermal atomic absorption spectrometry (ETAAS) [8], atomic fluorescence spectrometry (AFS) [9], inductively coupled plasma mass spectrometry (ICP-MS) [10] and electrothermal vaporization coupled to ICP-MS (ETV-ICP-MS) [11] were already employed for total Hg determination in the samples.

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DOI: 10.22146/ijc.23092

The hydride generation of cold vapor of mercury coupled to spectrometric techniques is usually employed. Cold vapor-atomic absorption spectrophotometry (CV-AAS) is the most widely used technique for the determination of Hg because of its main advantages including the possibility of separation of the analyte from its matrix with the inherent minimization of matrix interferences and the possibility of analyte pre-concentration, leading to increased measurement and the results obtained even at the low levels of concentration [12-14].

The fundamental principle of determination of Hg in the samples is the formation of metal-hydride by reductant $SnCl_2$ or $NaBH_4$ in gas-liquid separator placed in hydride generator system and produce Hg-hydride. The formed Hg-hydride will then go to a quartz cell placed on either the AAS is driven by a carrier gas of argon to read absorption value [15-16]. The atomization occurred in the quartz cell is caused by the light from the hollow cathode that passes it through. The advantage of this method is that the detection limit and sensitiveness can be enhanced because the metal has been separated from each other in their hydride forms [17].

Analysis of Hg in Laboratory of Environment Control, P.T. Badak NGL-East Kalimantan has been using the CV-AAS method with argon as a carrier gas. Argon gas is an inert gas that has high enough purity, but quite expensive and takes times because it must be purchased from a partner. Frequent reliance on the availability of argon gas, if there is no supply of argon gas, analysis cannot be done immediately. Based on, raised a new idea for replacing the carrier gas with cheaper gas and does not depend on the procurement process. In this case, nitrogen gas is already available in the laboratory because it is one of the products of the utility unit in P.T. Badak NGL refinery and used for the LNG/LPG process usage.

In this research, it has been developed a method using nitrogen gas as a carrier gas. Nitrogen gas is obtained from the refinery processes, namely P.T. Badak NGL #29th plant utility. Therefore, a study to determine the effect of utilization of nitrogen as a carrier gas in the determination of Hg using CV-AAS method needs to be conducted as well as to determine the validity of the developed method for appropriate used in the analysis.

EXPERIMENTAL SECTION

Materials

A solution of CRM Mercury in Water (Low Level PT-2) RTC Number: CS-1310 LOT: 017 937 with a concentration value of 2.48 ± 0.04 µg/L and Acceptance Limits of 2.15–2.81 µg/L, Hg stock solution 1000 mg/L, $SnCl_2$ (concentration series of 6-14% w/v), HNO_3, HCl, nitrogen gas; all of the reagents were of analytical-reagent grade (E. Merck), and double-distilled water.

Instrumentation

Spectrophotometer AA 240-FS variant complete with Vapor Generator Accessory VGA–76. Other equipment such as analytical balance, the volume pipettes, stopwatch, oven, hot plate with stirrer, was used for all measurements.

Procedure

Quality determination of nitrogen gas

Nitrogen gas was stored in pressurized gas cylinder mounted regulator and equipped with a filter and moisture trap, then analyzed using gas chromatography instrument.

Preparation of blank solution

The prepared blank solution is distilled water containing 5% (v/v) HCl. Double-distilled water 300 mL was entered to 500 mL volumetric flask, add 65 mL 37% HCl and matched in volume with double-distilled water, whipped until homogeneous.

Preparation of Hg stock solution 1000 mg/L

Amount of 0.1354 g $HgCl_2$ was diluted with 70 mL double-distilled water, added with 1 mL HNO_3 and it was diluted to 100 mL with double distilled water.

Preparation of CRM mercury standard solutions in Water (Low-Level PT-2) RTC Number: CS-1310 LOT: 017 937

CRM standard solution of 10 mL was piped and diluted in 1000 mL double-distilled water and 1 mL HNO_3. This solution has a concentration value of 2.48 ± 0.04 µg/L and acceptance limits 2.15–2.81 µg/L accordance with the value stated in the Certificate of Analysis.

Preparation of series Hg CRM standard solution in Water (Low-Level PT-2) RTC Number: CS-1310 LOT: 017 937

A certain volume of Hg CRM standard solution was diluted in double-distilled water with adding concentrated HNO_3 to obtain series of concentration (1.24, 1.86, 2.48, and 3.72 µg/L).

Determination of reading delay time

Read delay time was measured for 0–60 sec after standard solution added into mixing system (in the reaction coil). The maximum absorbance was subsequently used to the analytical performance test methods of Hg determination.

Determination of $SnCl_2$ concentration as reductant

Series concentrations of $SnCl_2$ (5 to 12% (w/v)) was prepared and measured their absorption. Maximum absorbance then subsequently used to the analytical performance test methods of Hg determination.

Determination of HCl concentration

Concentration of HCl (2 to 7% (v/v)) solutions were measured their absorption. Maximum absorbance then subsequently used to the analytical performance test methods of Hg determination.

Calibration curves and regression line equation

Hg standard with series concentrations of 0.0 - 12.0 µg/L and Hg CRM concentrations of 0:00; 1:24; 1.86; 2:48; 3.72 µg/L were measured by CV-AAS to obtain absorbance values.

Repeatability test

Repeatability test is performed by 10 times measuring standard solutions of Hg 6.0 and 9.0 µg/L and Hg CRM standard solutions in Water (Low-Level PT-2) RTC Number: CS-1310 LOT: 017 937.

Accuracy test

Accuracy test was done in two ways: first, by measuring 10 times Hg standard solutions of 6.0 and 9.0 µg/L then calculated % recovery. The second way is by measuring 10 times Hg Certified Reference Material (CRM) solution by CV-AAS, then calculating the average and compared with specified Certified Value in the Certificate of Analysis Standards.

Limit of detection and quantization

Detection and quantitation limits were determined by measuring double-distilled water reference solution with spike until Hg levels up to 0.1 mg/L, and 5% (v/v) HCl and analyzed 10 times by CV-AAS.

RESULT AND DISCUSSION

Nitrogen Gas Quality Analysis

Nitrogen gas obtained from PT Badak NGL #29th plant and analyzed first by using HP 6890 Agilent gas chromatography before it is used as a carrier gas in Hg analysis by the CV-AAS method. Gas chromatography (GC) is a widely used method for determining the composition of complex mixtures of chemical species in the gaseous phase. In the course of a GC analysis, the components of the mixture are separated on the basis of differences in the rate at which they are carried through a stationary phase by a mobile gas phase [18]. The results show that nitrogen gas has very high purity up to 99.9495%.

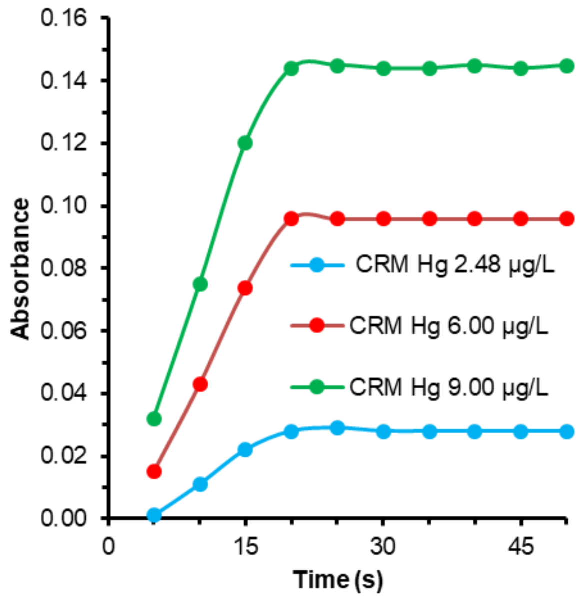

Fig 1. Reading delay time variation chart

Read Delay Time

Read delay time is a required time for Hg vapor flowing through VGA pipe tube of reaction coil to absorption cells until absorbance signal reading is done. The reaction coil is a mixing place of the sample, H^+ and $SnCl_2$ reductant, Hg^{2+} ions are reduced to Hg^0 and free atoms Hg^0 gaseous is going to absorption cell for absorbance measurement [16]. Time delay greatly affects the low and high of absorbance. Determination of the delay time by measurement of absorbance from Hg standards 6.00; 9.00 µg/L and Hg CRM 2.48 ± 0.04 µg/L with a time delay variation 5–50 sec as shown in Fig. 1. The Optimum absorbance of reading time delay was in 20 sec.

Influence of $SnCl_2$ Concentration as Reductant

The generation of Hg cold vapor depends on the addition of a suitable amount of reducing agent, since mercury is found in solution in the form of Hg(II) ions and needs to be reduced to gaseous elemental Hg [6]. $SnCl_2$ was employed for this purpose. Determination of the influence of $SnCl_2$ concentration in reducing Hg^{2+} ion into Hg^0 was performed by optimization test with a varying $SnCl_2$ concentration of 5–12% (w/v) with H^+ and Hg standard concentration made permanent. The results of research shown in Fig. 2. The optimal concentration of $SnCl_2$ gives a maximum absorbance of

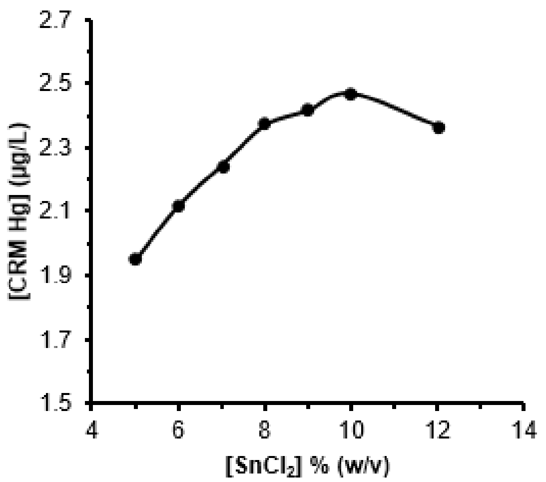

Fig 2. Influence of $SnCl_2$ concentration

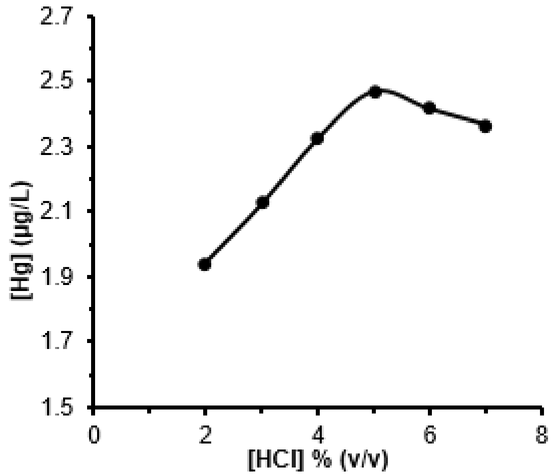

Fig 3. Influence of HCl concentration

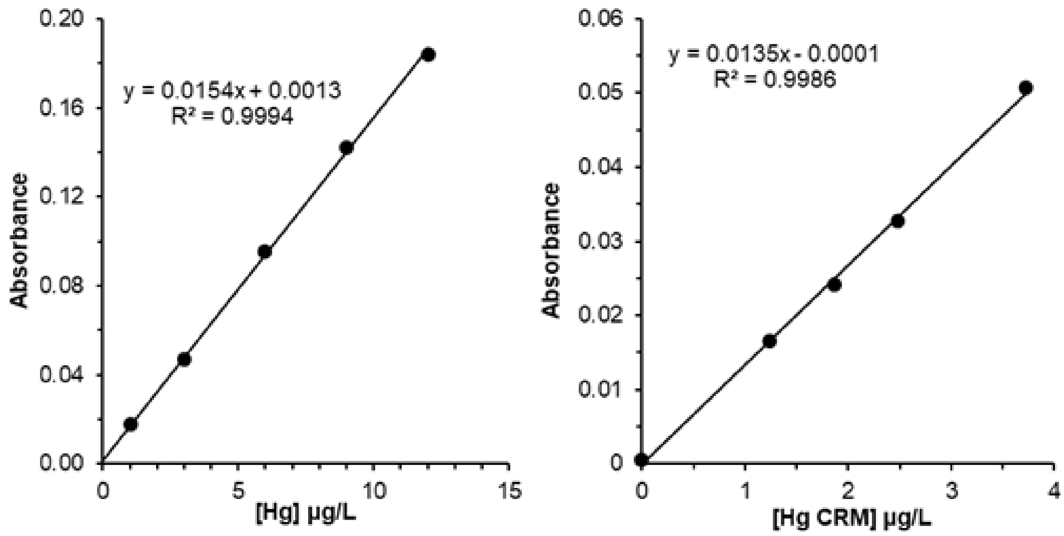

Fig 4. Calibration curve of (a) Hg standard and (b) Hg CRM

Hg CRM 2.48 ± 0.04 µg/L was 10% (w/v). Therefore, a 10% (w/v) $SnCl_2$ solution was employed in all further experiments.

Influence of Acid Concentration

The vapor generation of Hg also depends on the acidity of the medium since the decomposition of $SnCl_2$ into hydrostanno intermediates, which are responsible for the reduction of Hg(II) ions, is accelerated in acidic medium [19]. Hence, to keep the medium acid sufficient for promoting suitable Hg vapor evolution, HCl solution was added to the sample (or standard solution) before addition of $SnCl_2$ solution. In the research stage, HCl as acids prepared in several concentrations 2–7% (v/v), while standard concentrations of Hg and $SnCl_2$ reductant made permanent. The results obtained in this experiment (Fig. 3) showed that the highest response could be achieved when HCl concentration was 5% (v/v) with produced to highest Hg CRM 2.48 ± 0.04 µg/L. When the HCl concentration was higher than this value, a decrease of Hg signals was verified. In view of these results, a 5% (v/v) HCl solution was selected for the method.

Determination of Calibration Curves

Determination of calibration curve and the regression line is done by measuring the Hg standard and Hg CRM in various concentrations. Measurement results are shown in Fig. 4. The concentrations of Hg standards are in the range 1.0–12.0 µg/L. The linear regression equation: y = 0.0154x + 0.0013 with coefficient of correlation (R^2) = 0.9997 (Fig. 4a). Hg CRM calibration data is shown in Fig. 4b can be seen that the area of the linear range of concentration CRM

Table 1. Measurement of Hg standard and Hg CRM for repeatability test

Measurement	Hg Standard 6.0 µg/L	Hg Standard 9.0 µg/L	Hg CRM 2.48 ± 0.04 µg/L
2	6.162	9.265	2.5236
3	6.172	9.283	2.4919
4	6.114	9.258	2.5101
5	6.133	9.268	2.5248
6	6.132	9.290	2.5098
7	6.125	9.274	2.4917
8	6.113	9.272	2.5207
9	6.147	9.279	2.4910
10	6.138	9.248	2.5079
Mean (X)	**6.134**	**9.271**	**2.5083**
SD	**0.022**	**0.012**	**0.0138**
% RSD	**0.351**	**0.131**	**0.5495**
CV Horwitz	**34.443**	**32.367**	**39.4050**
2/3 CV Horwitz	**22.962**	**21.578**	**26.2700**

Table 2. Measurement of Hg standard and CRM solution

Measurement	Hg 6.0 µg/L		Hg 9.0 µg/L		Hg CRM 2.48 ± 0.04 µg/L	
	Measured	% Recovery	Measured	% Recovery	Measured	% Recovery
1	6.105	101.75	9.270	103.00	2.5115	101.27
2	6.162	102.70	9.265	102.94	2.5236	101.76
3	6.172	102.87	9.283	103.14	2.4919	100.48
4	6.114	101.90	9.258	102.82	2.5101	101.21
5	6.133	102.22	9.268	102.98	2.5248	101.81
6	6.132	102.20	9.290	103.22	2.5098	101.20
7	6.125	102.08	9.274	103.04	2.4917	100.47
8	6.113	101.88	9.272	103.02	2.5207	101.64
9	6.147	102.45	9.279	103.10	2.4910	100.44
10	6.138	102.30	9.248	102.76	2.5196	101.60
Mean± SD	**6.134± 0.022**	**102.24±0.36**	**9.271±0.012**	**103.01±0.14**	**2.5095±0.013**	**101.19±0.55**

Hg is 1.24–3.72 µg/L, the obtained the linear regression equation are y = 0.0135x - 0.0001 with a coefficient of correlation (R^2) = 0.9986. The measurement results of Hg standard and Hg CRM very good for Hg analysis, shown by the coefficient of correlation (R^2) are > 0.995 [20-21].

Repeatability Measurement

Repeatability is determined by measuring the concentration of Hg standard solution 6.0 and 9.0 µg/L and Hg CRM solution 2.48 ± 0.04 µg/L repeatedly with optimum conditions. Table 1 showed, % RSD of Hg standard solution 6.0 µg/L was 0.351% < 22.962, % RSD of Hg standard 9.0 µg/L was 0.131% < 21.578 and % RSD of Hg CRM solution 2.48 ± 0.04 µg/L was 0.5495% < 26.2700. All of % RSD of each Hg standard < 2/3 of CV Horwitz. This result indicated the good repeatability and acceptable measurement.

Determination of Accuracy

Accuracy is the closeness of analysis data with actual values. Accuracy value is determined in two ways: the first way is to measure the concentration of Hg standard solution 6.0 and 9.0 µg/L, and then % recovery value was calculated. Table 2 showed % recovery measurement of Hg standard 9.0 µg/L was 103.01 ± 0.14 and % recovery measurement of standard 6.0 µg/L was 102.24 ± 0.36. Each Hg standard result was in the range of required recommendation % recovery is 95–105% [21], and the accuracy was accepted.

The second way is to measure standard of Hg CRM 2.48 ± 0.04 µg/L repeatedly, then by comparing the mean of measurements with CRM values and acceptance limits stated in the certificate of CRM, which was shown in Table 2. The Mean Value of CRM was 2.5095 ± 0.0130 µg/L with % recovery was 101.19 ± 0.55 and appropriate in the value of CRM certification limits 2.48 ± 0.0383 µg/L and accordance within the concentrations range of CRM acceptance limits were 2.4417 to 2.5183 µg/L, and the accuracy was accepted.

Determination of Limit of Detection and Quantization

Limit of detection (LOD) is determined by measuring the smallest absorbance value which still can be defined and distinguished from signals given by

Table 3. Measurement of blank solution

Measurement [Hg] (0.10 µg/L)	Absorbance	Hg Concentration (µg/L)
1	0.0015	0.0130
2	0.0013	0.0000
3	0.0015	0.0130
4	0.0015	0.0130
5	0.0015	0,0130
6	0.0015	0,0130
7	0.0014	0.0065
8	0.0014	0.0065
9	0.0016	0.0195
10	0.0017	0.0260
Mean (X)		**0.0123**
Standard Deviation (SD)		**0.0071**
LoD = X + (3xSD)		**0.0338**
LoQ = X + (10xSD)		**0.0838**

blank with some measurements [22]. Table 3 showed that the limit of detection was 0.0338 µg/L and the limit of quantitation was 0.0838 µg/L. This result showed the lowest concentration of sample that can still be detected by instruments and the analysis methods was0.0338 µg/L while the lowest concentration of analyte that can be determined with acceptable accuracy was 0.0838 µg/L.

CONCLUSION

The results of the research showed that the nitrogen gas can be used as a carrier gas replacing

argon gas in the determination of Hg ions, which are shown the repeatability values as % RSD < 2/3 CV Horwitz values, the LOD was 0.0338 µg/L and the LOQ was 0.0838 µg/L. The accuracy of this method is good shown by a recovery percentage was 102.24%, the CRM readings are 2.5095 µg/L and accordance within the CRM certificate of the range 2.48 ± 0.04 µg/L. Based on this research, the nitrogen gas can be used as a carrier gas for the determination of Hg ions in the samples by using CV-AAS with valid results.

ACKNOWLEDGEMENT

The authors would like to thank the Chairman and staff of P.T. Badak NGL Bontang, East Kalimantan for the laboratory facilities and the samples provided in the implementation of this research.

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