Determination of Mercury in Sweet Gas by Atomic Absorption Spectrometry Using Gold Amalgam Collection: A Case Study in the North Gas Company, Iraq

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Abstract

Mercury is recognized as a metallic constituent in natural gas. It exists in natural gas (sweet gas is medial Output) and causes failure for some equipment in the lines products. So, it is necessary to determine the nanograms of mercury in sweet gas samples by using gold-amalgam collection and analysis by atomic absorption spectrometry (Vapor-method). In this method, the calibration curves are linear and ranging from 0.01 to 1000 ng of mercury. In sweet gas measurement, the range is wide enough for work with the correlation coefficient of 0.9999. The detection limit for the amalgam method (three times the standard deviation of a blank determination) is determined to be 0.003ng for samples of mercury. Vapor collected on sorbent tubes contained 80mg of porous gold-coated. The accuracy of this procedure is confirmed by determination of the standards taken form standard box of mercury MB-1 as unknown concentration. Finally, the range of mercury in sweet gas supposed to be from 2.48 - 8.9 nanogram per normal cubic meter.

Key Words: Mercury, Atomic Absorption Spectrometry, Gold-amalgam Collection.

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Introduction

Due to the hazards of mercury exposure, it was determined in the workplace air to realize the rate of air contaminated by liquid collection using permanganate oxidation with cold vapor atomic absorption spectrometry (CV-AAS). In the important natural gas fields, to conduct the ecological geochemistry evaluation, adsorption collection for geogas survey is proposed by researchers for the first time to collect the trace elements in the natural gas. Furthermore, mercury was found out successfully as trace elements using inductively coupled plasma technique (ICP) (Duoyi *et al*, 2008).

Generally, sweet gas is one of the natural gas middle products from the north gas company located in Kirkuk/ Iraq. It is consisted of about 91% of light hydrocarbons (C1 and C2), which separate thereafter to produce sales gas that provides electric generation stations to use as a fuel to produce electricity.

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Knowing the amount of mercury in natural gas is essential because extra mercury existing upper the limited amount may lead to damaging aluminum that covers the heat exchangers, which consequently costs a lot. Since mercury reacting with aluminum and resulting amalgamates, which in consequence causes damaging of the heat exchangers. Eventually, lead to gas leakage and let to total removing mercury from downstream gas (Corvini *et al*, 2002). The amount of mercury could not be signified exactly because it varies from one gas well to another. In this respect, studies showed that the amount of mercury is not steady and defer from time to time (Markovs & Clark, 2005).

In the literature, for gas and condensate samples, different mercury analysis techniques have been proposed, which determine either elemental mercury or total mercury. Generally, in natural gas, mercury is almost available in elemental form. However, organomercury compounds in condensates and petroleum liquids are significant and could be a predominant form of mercury (Edmonds *et al,* 1996) For mercury vapor measurement, the amalgamation based analysis is widely used as a sensitive method. Additionally, the method uses a preheated second mercury trap by capturing mercury vapor and passing it through interfering substances (e.g., volatile organic compounds). Besides, it is also known as double amalgam method. In the second step, up to at 700 °C, the mercury trap is heated to adsorb mercury vapor for CVAAS measurement (Takaya *et al*, 2006; International Standard 20552, 2007) For mercury adsorption, using of gold-coated beads helps to preconcentrate ultra-low average concentration in gas samples over big volume from 80 to 100 liters

Experimental Part

1) Apparatus

To concentrate the mercury in sweet gas directly, the mercury analyzer WA-4 Nippon instruments corporations are applied by using mercury collector tube 12cm long 0.25-in outside diameter yo to be used for sorbent (gold-coated silica). Generally, each Nippon instruments corporation contains a single section of porous gold-coated stored in a glass tube with a butyl rubber stopper. Additionally, it contains 80 mg of gold-coated silica retained by small quartz wool plugs. It is worth mentioning that the collector tubes precondition is desirable before sampling by heating to 700 °C by the mercury analyzer and passing air through them in a flow rate of 0.5 L/min to reduce the mercury blank. Furthermore, the Tedlar bag was used to bring the samples from the sample point. Two Tedlar bags were used where each bears 85 - 95 liters of sweet gas. It is important to take in case of filling the Tedlar bag to avoid tearing under the pressure of the gas. A flow-stabilized pump (Nippon instruments) was used to make the gas sample pumps through the collector tube. The tube was properly connected between the Tedlar bag through the PS-4 pump vacuum to a dry gas meter. Additionally, the gas meter was used to measure the total volume of the gas sample through the collector tube. Then, the flow rate was controlled by the flow-stabilized pump at a rate of 1 L/min. After that, the gas sample was exhausted through the dry gas meter to a well-ventilated hood.

WA-4 analyzer contents of two gold-amalgam units, which comprises of two heaters, a gas washer and charcoal filter. They are connected to an analyzer unit employing a cold vapor atomic absorption spectrometer. Figure 1 illustrates the double gold an amalgam system with cold vapor atomic absorption spectrometry (CVAAS). The system is controlled by WA-4 data analysis software installed on the Windows XP operating system.

2) Reagents

To make a calibration curve, an analytical mercury reagent standard gas from MB-1 standard box was used. Buffer solution pH 7 (1-1) (one volume of buffer and another of distilled water) was used into scrubbing bottle in the electronic cooling unit (a 500 µl aliquot of the headspace over mercury in a sealed vial is equivalent to 10.75 at 26 °C). The temperature must be closely regulated because the vapor pressure of mercury is dependent on the temperature. Table 1 lists the quantity of mercury contained in 1ml of gas at various temperatures.

Table 1. Quantity of mercury in 1 ml of gas with different temperatures

Temperature (°C)	ng mercury in 1 ml
21.0	14.315
23.0	16.869
25.0	19.852
27.0	23.289
28.0	25.198

3) Preliminary Studies of the Detection Mercury in Sweet Gas

Getting a representative sample from a process line requires a special sample. Figure 1 shows sampling point configuration for Hg analysis that installed in one of the sweet gas points in production unit (has 406 psi pressure) related to the north gas company, Kirkuk, Iraq. The sampling point consists of 1200 psi regulator to control the high pressure of the sample point. It is supported by a Millipore filter to prevent coarse particles passing through the regulator. The reason is that any amount of solids in this system may cause stopping analysis for a long time. The inlet point of the regulator was connected to the sample point. Additionally, the outlet point was connected with Tedlar bag by clear polyvinyl laboratory tube, which was the connecting tool between parts of the sampling system. A Tedlar bag with a capacity of 85 - 95 liters gas was supported with plastic valve as inlet point. After collecting sweet gas by the Tedlar bag, the later was connected to M160-Hg collector tube. Furthermore, the outlet of the later was connected to a counter flowmeter to calculate the whole volume in liter passing through the sample system. Later, the volume was converted to normal cubic meter. The main reason is the sample point was at pressure, and the mercury analysis was done at atmospheric conditions.

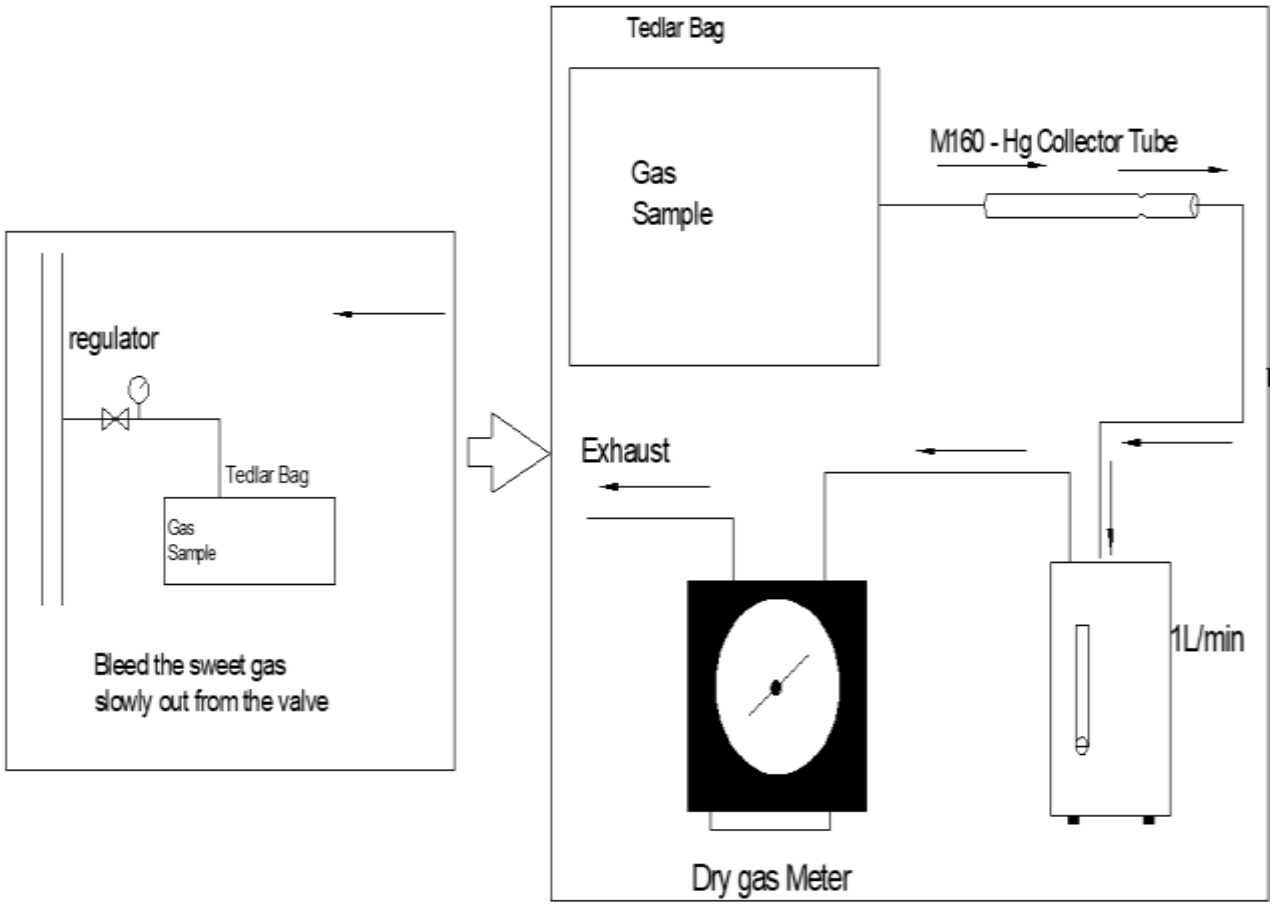

Figure 1. Sampling point configuration

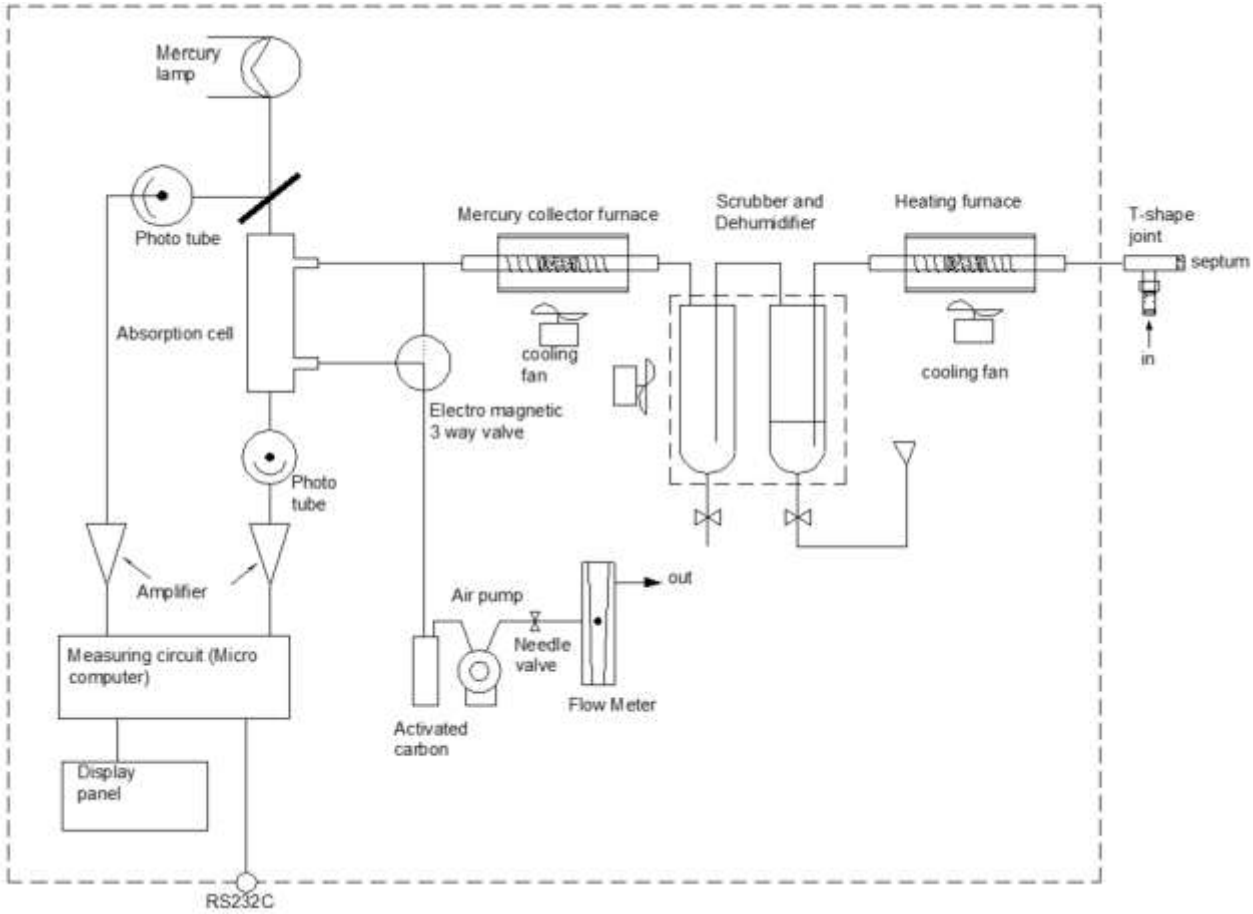

Figure 2. Flow chart

Results and Discussion

As illustrated in Figure 3, a linear calibration graph was obtained by plotting integral in absorbance-seconds against ng mercury. The calibration graph has a correlation coefficient of 0.9999 and relative standard deviation RSD% between (2.1 - 5.0). Table 2 lists the assigned parameters in the operations by the manufacturer. Whereas, Table 3 summarizes the standard concentrations and the response for the calibration curve. Standard 0.00 refers to no injection was done, and only the ear flow has proceeded.

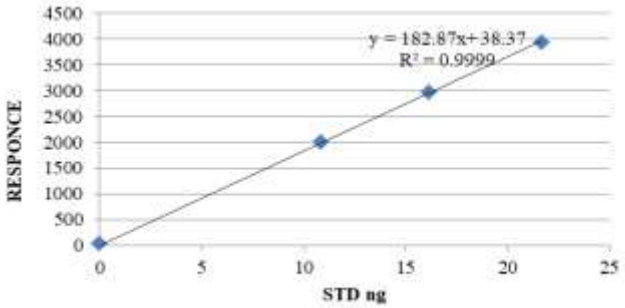

Figure 3. Calibration curve

Table 2. Parameter sets

Parameter	Value
Wavelength	253.7 nm
Slit width	0.7 nm
Background correction	On
Absorption cell temperature	100 ℃

Table 3. Standards and their absorptions

No.	Standard	Integral
1.	0.00	32.859
2.	10.873	2003.7
3.	16.134	2973.2
4.	21.681	3940.3

Table 4 presents the analytical calculation of the calibration graph and the range that depend on gaining the limit of detection (LOD) and RSD%. Limit of detection was obtained by measuring the blank ten times at the 253.7 nm. Furthermore, a wide range of linearity has been obtained from 0.01 to 1000 ng, and RSD% was obtained for three replicate. Note that the standards were taken from the MB-1 mercury standard box at room temperature in the range 17.9 - 18.5 ℃. The reason was that the temperature fluctuated the reading of

the instrument. Table 5 outlines the parameters obtained by the mercury analyzer instrument. It consists of the integrals for the standards, and some reads of the significant concentration of mercury were taken from the MB-1 box and reading for blanks.

Table 4. Analytical characteristics of mercury standard

Parameter	Characteristic
Calibration equation	y = 182.87x+ 38.37
Linear analytical range (ng)	0.01 - 1000
RSD % (n*= 3)	2.1 -5.0
LOD ng	0.001

n= number of measurements

Table 5. Data gained by standards and samples

No.	Sample name (gas)	Standard (ng)	Integral	Mercury (ng)
1.	STD	0.00	32.859	
2.	STD	10.873	2003.7	
3.	STD	16.134	2973.2	
4.	STD	21.681	3940.3	
5.	16.4 ng		2901.7	15.57
6.	17.1 ng		2920.4	16.12
7.	18.2 ng		3001.5	15.6
8.	Blank		15.51	
9.	Blank		40.117	
10.	Blank		23.04	

The Fluctuation in temperature causes a relative difference during the sequential analysis. As listed in Table 6, the Erel% was ranged from (-5.0) to (-9.4), and the recovery % was varied from (91) to (94.9). Finally, Table 7 presents the mercury concentration of sweet gas samples that were passed through the collector tube at laboratory temperature at the rate of 1 L/min. Consequently, we can limit the result between (2.48 – 8.9) ng/m3.

Table 6. Data gained by standards and samples

Actual amount	Analyzed amount	Abs	Er%	Recovery %
16.4	15.57	2901.7	-5.0	94.9
17.1	16.12	2003.7	-5.7	94.2
17.3	15.68	2973.2	-9.4	91
16.9	15.84	3940.3	-6.3	94

Table 7. Mercury concentration in sweet gas samples

Passed gas L	Instrument reading (ng)	Hg in ng/m3
86	0.43	4.3
137	1.22	8.9
80	0.236	2.95
88	0.371	4.21
88	0.27	3.1
93	0.456	4.9
93	0.231	2.48
88	0.232	2.63
86	0.540	6.4

Conclusion

To conclude, by using mercury analyzer WA-4, it is possible to determine the amount of mercury in sweet gas, which is an outcome of the production line in natural gas company, Kirkuk, Iraq. The findings demonstrated that the method is accurate and could be used as routine method for determining mercury in nanoparticle concentration with a good response. Molecular sieve coated by gold amalgam is a suitable medium to absorb mercury particles from gases, which could be separate thereafter by heating and detecting by absorption cell. The sample preparation procedure required specific equipments to perform that leads to direct analysis. Finally, the amount of mercury in sweet gas is less than 10 ng/m^3.

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