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"An innovative approach to reuse the costly Silver Diethyl Dithio Carbamate (SDDC) solution in the analysis of Arsenic in water samples"

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Abstract- In the analysis of Arsenic in water samples the Silver Diethyl Dithio Carbamate being used is a costly chemical and its solution is prepared in chloroform. This yellow colour reagent is used to absorb AsH_3 gas produced in the reaction flask. It is absorbed by the yellow coloured Silver Diethyl Dithio Carbamate solution containing in u-tube and changed into reddish colouration. The reddish colour intensity is increased by the increase of arsenic present in the water sample which is measured by spectrophotometer at the wavelength of 520 nm. Generally arsenic is not found in most of the samples of drinking water in that case the formation and absorption of AsH_3 does not occur in the solution of Diethyl Dithio Carbamate as the reading shows '0'. Thus the solution of SDDC is remaining as such without any change in colour and that can be reuse for further analysis of arsenic, if collected instead of throwing it away. Thus under the utilization of the waste the utilization of '0' Arsenic containing SDDC is successfully found useful and satisfactory for further determination of Arsenic. The used SDDC is also used as blank zero to minimize any error. Precautionary it should be filter by 40 no. Whatman filter paper before being reused to avoid any turbidity formed on keeping the used solution of SDDC. Thus the SDDC solution should be very clear to use.

Keywords- Chloroform, SDDC, spectrophotometer.

INTRODUCTION

Arsenic, a naturally occurring toxic metalloid is ubiquitously found in the environment. It is the 20th most abundant metal in the Earth's crust and is one of the major constituent of more than 200 minerals like sulphides, arsenates, arsenites and oxides (**Joshi *et al.* 2016)**. The average abundance of Arsenic in the earth's crust is 1.8 ppm, in soil it is 5.5-13 ppm, in streams it is less than 2 ug/l and in ground water it is generally less than 100 ug/l. Naturally it occurs in the form of sulphide minerals like pyrite, arsenic is used in alloys with lead in storage batteries and its compound used in pesticides and wood preservative. In aqueous form it occurs as arsenite, arsenate by mineral dissolution, industrial discharges and pesticides **(Rodger B. Baird *et al.* 2017)**. The arsenite is more toxic than arsenate. For aquatic life its concentration should not exceed 72ug/l and the maximum should not 140ug/l.

Principle:

Arsenic is a non-metallic constituent, present naturally in groundwater due to some minerals and rocks (**Tahir *et al.* 2012)**. The arsenite containing trivalent arsenic and arsenate containing pentavalent arsenic, is reduced (As^{+5}-As^{+3}) by adding KI and $SnCl_2$ solution to arsine AsH_3 in an aqueous medium **(Rodger B. Baird *et al.* 2017)**. The generated arsine is swept by a stream of free hydrogen produced by the reaction of zinc and conc. HCl added from the reaction vessel through a scrubber containing glass wool or cotton wetted with lead acetate solution in to an absorber U tube containing Silver diethyl Dithio Carbamate and morpholine dissolved in chloroform. The intensity of red colour develops is measured at 520 nm. The limit of Arsenic estimation is 0.001 mg/lt i.e. 1 ppb.

Apparatus

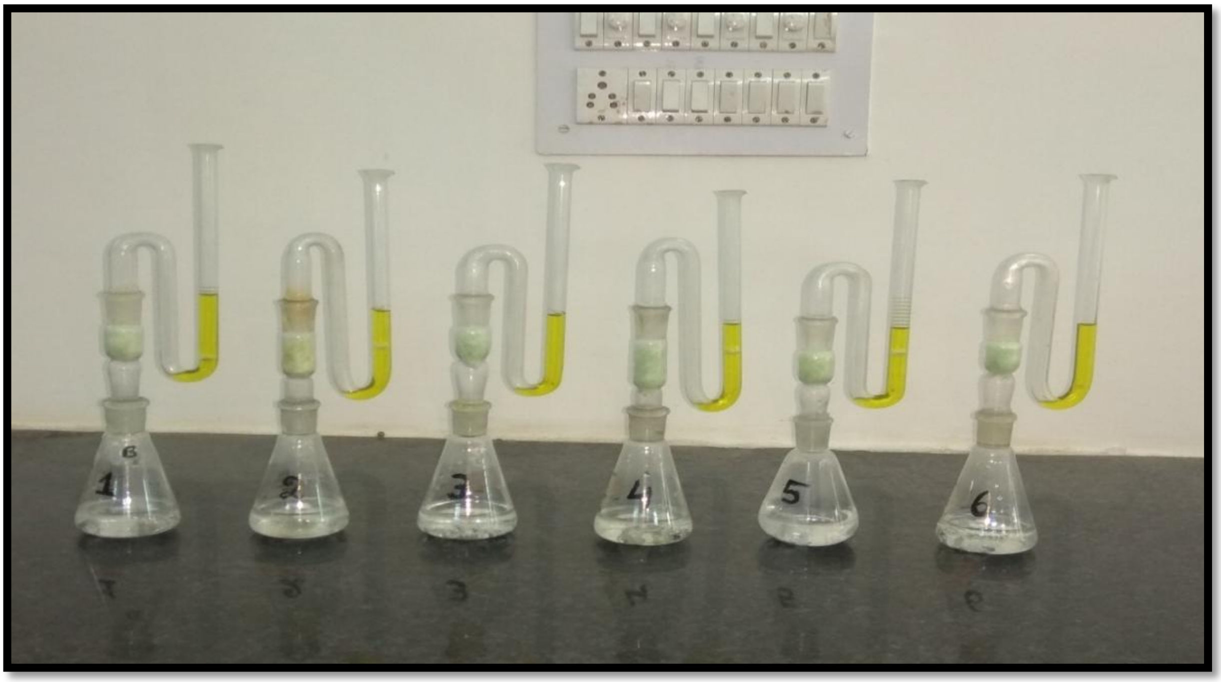
1. Arsine generator assembly complete set as shown in figure 1 which consist of reaction flask i.e. Arsine generator, scrubber and absorber tube.
2. Fume hood.
3. Spectrophotometer having 520 nm wave length.
4. Cells for spectrophotometer of 1-cm or 5-cm with cover to prevent $CHCl_3$ evaporation.
5. Glass wool, Vacuum grease **(Trivedy and Goel, 1986)**

Reagent

1. Reagent grade water.
2. Hydrochloric acid.
3. Lead Acetate solution 10% in D.W.

4. Silver diethyl Dithio Carbamate solution- 1 ml morpholine in 70ml chloroform then add 0.3g SDDC$[Ag\ SCSN\ (C_2H_5)_2]$ Shake in a stopper flask to dissolve, than dilute to 100ml with $CHCl_3$, filter and then store in tightly closed brown bottle in a refrigerator. It is necessary to compare with used reagent of SDDC.
5. Standard CRM grade Arsenic solution of 1000 mg/lt.
6. Dilute solution of arsenic of different concentration i.e. 5ppb, 10ppb, 20ppb, 50ppb, 100ppb.
7. Chloroform.
8. Zinc flex.
9. KI solution 15% in D.W.
10. $Sncl_2$ solution 40% in conc. HCl **(Trivedy and Goel, 1986).**

Fig. 1: Arsine Generator and Absorber Assembly



Procedure

1. Preparation of Arsine generator assembly – Dip glass wool into 10% lead acetate solution and make it almost dry and filled it into scrubber. The upper part of scrubber is also filled with loose dry glass wool. All the joints make greasing with vacuum grease to make assembly leak proof. Ultimately filled the absorber U-tube with 5ml of silver diethyl dithio carbamate solution which is already used and here it is again reused parallel to new one.
2. Processing arsine generator – In a 100ml conical flask with mouth of ground glass, 35ml of water sample is added followed by addition of 2ml of 15% KI solution and then 0.5ml of 40% $Sncl_2$ solution in Conc. HCl. Keep it for 15 minute to reduce As^{+5} to As^{+3}.
3. Arsine generation and its absorption- After 15 minute of reduction reaction about 3.5gm of zinc flex is added into arsine generator and immediately close the assembly as shown in figure 1. The arsine gas (AsH_3) starts forming and coming out through glass wool kept in scrubber and absorption takes place in silver diethyl dithio carbamate solution kept in absorber U-tube. The other gas formed goes out through the open mouth of the U-tube. The complete reaction takes place within 20-30 minute.

Measurement*:* The silver diethyl dithio carbamate method determines inorganic arsenic when present in concentrations at or above 10ug/l. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver **(EPA, 1983)**. Pour arsine absorbed silver diethyl dithio carbamate solution from absorber into 5ml volumetric flask and make up the lose of volume with chloroform than from this flask pour the solution into a clean and dry spectrophotometer cell of 5cm and measure absorbance at 520nm against blank zero prepared in the same way using used silver diethyl dithio carbamate. Thus determined the concentration of arsenic in water sample directly in mg/lt from calibration curve/graph obtained with arsenic standards.

Preparation of standard graph/curve**:** Treat standard arsenic solution containing .005, .010, .020, .050, 0.100 ppb Arsenic as described earlier/above. Plot absorbance versus microgram arsenic in the standard. It will be a straight line graph feed it in the spectrophotometer for determination of Arsenic in water sample which gives direct reading/value of Arsenic in mg/lt. The same graph can also be prepared with used SDDC solution as per method developed.

Precaution: If lead acetate of glass wool becomes in effective in removing hydrogen sulfide (H_2S) mean it becomes gray or black remove and filled another glass wool in scrubber chamber of the apparatus.

Table -1: Comparative data obtained with this method standard arsenic solution of different concentration.

Sr. No.	**Quantity of arsenic taken in mg/l from CRM solution**	**Quantity of arsenic found in mg/l**	**Deviation**	**% Deviation**
1	0.010	0.011	+.001	10%
2	0.020	0.021	+.001	5%
3	0.050	0.048	-.002	4%
4	0.080	0.082	+.002	2.5%
5	0.100	0.102	+.002	2.0%

Table -2: Comparative data obtained with drinking water with prescribed original SDDC Solution.

Sr. No.	**Natural sample of drinking water with code**	**Arsenic found with original SDDC solution**	**Arsenic with used SDDC solution**	**Deviation**	**% Deviation**
1	76872	0.022	0.020	0.002	9.09
2	76873	0.047	0.045	0.002	4.25
3	76875	0.092	0.090	0.002	2.17
4	76876	0.089	0.085	0.004	4.49
5	76883	0.071	0.073	0.002	2.81

Table -3: Spike sample prepared for RSD value for Standard Arsenic solution.

Sr. No.	**Quantity of Arsenic taken**	**Quantity of Arsenic found**	**Mean Value**	**Deviation (d)**	**d^2**	**SD= $\sqrt{\sum d^2/n-1}$**
1	0.050 mg/l	0.048	0.0496	-.002	.000004	0.0017
2		0.051		+.001	.000001	
3		0.052		+.002	.000004	
4		0.049		-.001	.000001	
5		0.048		-.002	.000002	
					.000012	

Calculation:

$$\mathrm{RSD} = \mathrm{SD} \times 100 / \mathrm{Mean}$$

$$= 0.0017 \times 100 / 0.0496 \quad = 3.427$$

RESULTS AND DISCUSSION

There is no doubt to reuse the SDDC as the arsenic absorbing reagent having zero value of arsenic shown in previous set of analysis. In case of large number of water sample where arsenic analysis is done and arsenic is found zero a large quantity of SDDC is collected as 5ml per sample as waste reagent. The result obtained is equally good and satisfactory and found reproducible by all means. As shown in table 1, 2 and 3 so it is advisable to reuse the silver diethyl dithio carbamate solution instead of throwing in to sink after analysis because it remains as such without any change where arsenic is found in zero value. The same used SDDC is also used for blank zero. The used SDDC must be filter by No. 40 Whatman filter paper to avoid any turbidity formed during keeping the solution of used SDDC. The reaction between SDDC and AsH_3 is shown below

$$\mathbf{Ag\,[SCSN\,(C_2H_5)_2] + AsH_3 \longrightarrow As[SCSN(C_2H_5)]_3}$$

Interferences: There is no question of any interference because for blank zero the same used SDDC is being used in proposed method. Some time turbidity is appears in the SDDC solution then it is necessary to filter it by 40 no. whatman filter paper to get clear and almost transparent yellow solution before pouring into arsine absorber U- tube. H_2S gas evolve will absorb in lead acetate absorber glass wool contained in absorber.

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