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ANALYSIS OF ARSENIC FROM WATER BY SPECTROPHOTOMETRIC METHOD

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ABSTRACT

Arsenic compounds are widely used, have been recognized as toxicants. The arsenic contaminated drinking water Arsenic from water may be determined by many methods such as atomic adsorption spectroscopy (AAS), Inductively coupled plasma atomic emission spectroscopy (ICP-AES), electrochemistry and spectrophotometry with silver diethyldithiocarbamate. This article presents a study on the arsenic determination from water by spectrophotometric method based on molybdate reagent. This method poses high sensitivity and selectivity but has not been studied in detail. The obtained results have sugested the experimental optimum conditions for arsenic determination by spectrophotometric method using molybdate reagent. The method consists of three steps (i) arsinization of arsenic to producing AsH_3, (ii) $AgNO_3$, H_2O_2reagents oxidized AsH_3 to producing As(V) and (iii) the reaction of As(V) with molybdate reagent to produce molybdenum blue complex. The absorbance of molybdenum blue complex at the wave length of $\lambda = 878$ nm has been used for arsenic determination. The LOD and LOQ of the method are 2 and 7ppb respectively

INTRODUCTION

Arsenic compounds are widely used that have been recognized as toxicants. The arsenic contaminated drinking water can affect the human health (Smedley *et al*., 2002, Berg *et al*., 2001, WHO Fact Sheet, 2001). Because arsenic concentrations in drinking water far exceeding the guideline value of the World Health Organization (WHO) pose a serious health hazard to tens of millions peoples (Smedley *et al*. (2002). Arsenic and its compounds are reported to be carsinogentic, mutagenic and tetratogenic in nature (Smith *et al*., Perkin Elmer 1995). Arsenic from water may be determined by many methods such as atomic adsorption spectroscopy (AAS), Inductively coupled plasma atomic emission spectroscopy (ICP-AES), Electrochemistry and Spectrophotometry (Farnet *et al*., 2010, Dhara *et al*., 2004). The chemical reagents used for arsenic spetrophotometric method are ammonium pyrrolidine- dithiocarbamate, silver diethylditiocarbamate, methylene blue, alizarine Red S, methyl orange and molybdate. Arsenate ions in the water sample react with molybdate ions and with a suitable reducing reagent give blue color due to formation of heteropoly species containing both Mo(IV) and Mo(VI) that can be used for determination arsenic from water samples. This method is influenced by the phosphate species and other metallic ions presented in water sample that give the same color with molybdate reagent. The influence of these chemical compounds may be overcome by conversion of arsenic species to arsine (arsinization), evolved and trapped in solutions containing $AgNO_3$ and H_2O_2 to convert arsine into arsenate before determining them. The arsenate compound then reacts with molybdate reagent to form arsenomolybdate blue complex. This compomplex can be used for determining arsenic concentration by spectrophotometric measurement at the maximum wave length of 878 nm (Ve´ronique Lenoble *et al*., 2003 and Susanna Tsang, 2007). In this work, a detailed investigation of high sensitive spectrophotometric determination for arsenic from water was presented. The method consists of some steps such as the arsinization of arsenic species, oxidation of arsine and the formation of arsenomolybdate blue complex.

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MATERIALS AND METHODS

Chemicals

All chemical reagents imported from Germany Merck company include: H_3AsO_4, $NaBH_4$, H_2O_2 30%, $AgNO_3$,

H_2SO_4, $K(SbO)C_4H_4O_6.1/2H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$, and $(NH_4)_6Mo_7O_{24}.4H_2O$. The following stocks were prepared: As(V) solution of 1000 mg/L, $AgNO_3$ (0.01M) and the combined reagent (CR). The combined reagent were prepared according to the literature[5] as follows:

- Sulfuric acid solution 2.5 M: dilute 70 ml of sulfuric acid H_2SO_4 to 500 mL distilled water, denotes R_1.
- Antimony potassium tartrate solution: Dissolve 0.270g of antimony potassium tartrate $K(SbO)C_4H_4O_6.1/2H_2O$ in 100 mL distilled water, denotes R_2 .
- Ammonuim molybdate solution: Dissolve 10,0 g of ammonuim molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ in 250 mL distilled water and store in plastic botlle at 4^0C, denotes R_3.
- Ascorbic acid 0.1M: Dissolve 4.4 g of acsorbic acid $C_6H_8O_6$ in 250 mL of distilled water, denotes R_4.

Above reagents are mixed in the following proportions for 100 mL, 50 mL, 2.5 M of R_1+ 5 mL R_2 + 15 mL of R_3 + 30 mL of R_4.

Experimental methods

Arsinization of all arsenic species and arsine oxidation

The arsiniation of all arsinic species (to producing AsH_3) was carried out in the presence of $NaBH_4$ (solid) and HCl acid solution in the reaction vessel with stirred. The arsine gas with the N_2 carrier gas stream was filtered through a cotton layer impregnated with $(CH_3COO)_2$ Pb to enter then into the absorption part containing $AgNO_3$ and H_2O_2 solutions. Here the AsH_3 was oxidized to produce As (V), Fig. 1.

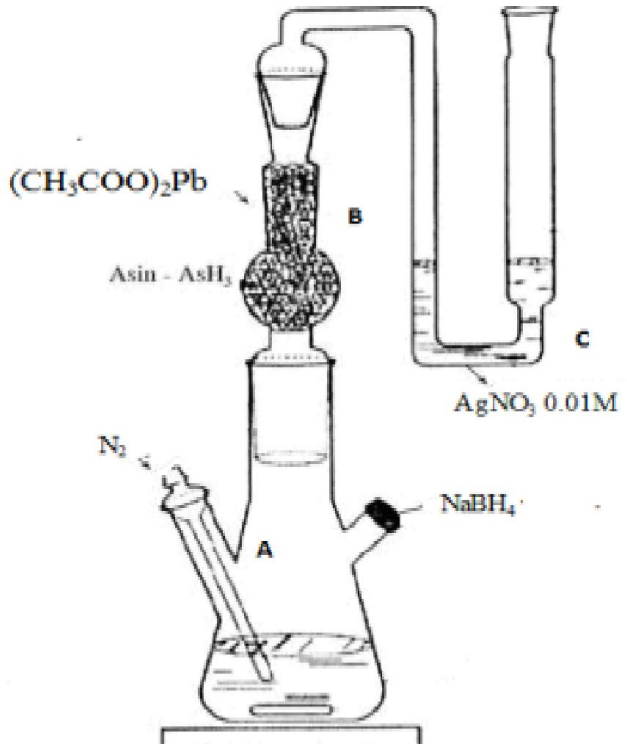

Fig.1. Kits for arsinization

A. Reaction vessel containing arsenic, $NaBH_4$, N_2 gas placed on a magnetic stirrer.

B. Filter of arsine gas by $(CH_3COO)_2$ Pb. Part of absorption and oxidation of AsH_3 gas.

Preparation of molybdenum blue

The obtained As (V) ions will react with the CR reagents in the other reactor vessel to producing arsenomolybdate and molybdenum blue complex. This complex was used to determination of arsenic concentration in the sample by spetrophotometric measurement at the wave length of 878 nm.

Analysis of arsenic concentration

Arsenic concentration was determined based on the measurement of absorbance of molybdenum blue complex at the wave length of 878 nm using spectroscopy UV-Vis Biochrom Libra (USA)

Experiments of determination of factors influencing on the arsinization process

According to the arsinization process, all oxidation chemicals ($AgNO_3$, H_2O_2), combined reagents, (CR), 5.0 mg/L, and blowing time of N_2 were kept constantly in the samples, the absorbance of the arsenomolybdate blue complex was measured at the wavelength of 878 nm with the varying the following factors

Infuence of the V_{HCl}

The experiments were carried out in the reaction vessel including arsenic solution of 50 mL, (0.10 mg/L), $NaBH_4$ solution, 15 mL, (1%), and the HCl (2M) acid volume varying from 7 to 13 mL. The experimental data were presented in the Table 1.

Table 1. The experimental data of samples

N_0	V_{As} (0.1 mg/L)	V_{HCl} 2M	V_{H2O}	V_{NaBH4} 1%	V_{CR}	n_{HCl}	n_{NaBH_4}	pH
	(mL)	(mL)	(mL)	(mL)	(mL)	(mmol)	(mmol)	
1	50.0	7.0	13.0	15.0	5.0	14.0	3.965	2.32
2	50.0	8.0	12.0	15.0	5.0	16.0	3.965	1.38
3	50.0	9.0	11.0	15.0	5.0	18.0	3.965	1.14
4	50.0	10.0	10.0	15.0	5.0	20.0	3.965	0.95
5	50.0	11.0	9.0	15.0	5.0	22.0	3.965	0.82
6	50.0	12.0	8.0	15.0	5.0	24.0	3.965	0.73
7	50.0	13.0	7.0	15.0	5.0	26.0	3.965	0.65

Influence of the ratio of (HCl+$NaBH_4$)/As

The experimental data of the samples are presented in the Table 2.

Table 2. The experimental data of samples

N_0	V_{As} (0.3mg/L)	V_{HCl} 2M	V_{NaBH4} 1%	V_{HCl} + V_{NaBH4}	V_{CR}	n_{HCl} + n_{NaBH_4}	n_{As}	pH
	(mL)	(mL)	(mL)	(mL)	(mL)	(mmol)	(mmol)	
1	50.0	7.0	10,5	17.5	5.0	16.775	2.0×10^{-4}	1.14
2	50.0	8.0	12,0	20.0	5.0	19.172	2.0×10^{-4}	1.05
3	50.0	9.0	13,5	22.5	5.0	21.568	2.0×10^{-4}	0.99
4	50.0	10.0	15,0	25.0	5.0	23.965	2.0×10^{-4}	0.96
5	50.0	11.0	16,5	27.5	5.0	26.361	2.0×10^{-4}	0.91
6	50.0	12.0	18,0	30.0	5.0	28.758	2.0×10^{-4}	0.87
7	50.0	13.0	19,5	32.5	5.0	31.154	2.0×10^{-4}	0.82

Influence of arsenic concentrations

The experimental data of the samples are presented in the Table 3.

Table 3. The experimental data of samples

N_0	V_{As} (0.01 mg/L) (mL)	$V_{HCl\ 2M}$ (mL)	$V_{NaBH4\ 1\%}$ (mL)	V_{CR} (mL)	pH
1	50.0	10.0	15.0	5.0	0.96
2	70.0	10.0	15.0	5.0	0.98
3	100.0	10.0	15.0	5.0	1,00
4	250.0	10.0	15.0	5.0	1.05
5	350.0	10.0	15.0	5.0	1.07
6	500.0	10.0	15.0	5.0	1.10
7	750.0	10.0	15.0	5.0	1.13

Influence of the N_2-blowing time

The experimental data of the samples are presented in the Table 4.

Table 4. The experimental data of samples

N_0	V_{As} (0.1 mg/L) (mL)	$V_{HCl\ 2M}$ (mL)	V_{NaBH4} 1% (mL)	V_{CR} (mL)	N_2 blowing (min)
1	50.0	10.0	15.0	5.0	10.0
2	50.0	10.0	15.0	5.0	15.0
3	50.0	10.0	15.0	5.0	20.0
4	50.0	10.0	15.0	5.0	25.0
5	50.0	10.0	15.0	5.0	30.0
6	50.0	10.0	15.0	5.0	35.0
7	50.0	10.0	15.0	5.0	40.0

Determining the optimum conditions of molybdenum blue formation

For all experiments, the absorbance of the arsenomolybdate blue compound was measured at the wavelength of 878 nm.

Influence of pH

The experimental data of the samples are presented in the Table 5.

Table 5. The experimental data of samples

N_0	V_{As} (2mg/L) (mL)	V_{CR} (mL)	V_{total} (mL)	pH
1	0	5	50	0.8
2	5	5	50	0.2
3	5	5	50	0.4
4	5	5	50	0.6
5	5	5	50	0.8

Influence of the ratio (V_{CR}/V_{As})

The experimental data of the samples are presented in the Table 6.

Table 6. The experimental data of samples

N_0	V_{As} (2mg /L) (mL)	V_{CR} (mlL)	V_{CR}/V_{As} (mL/mL)	V_{total} (mL)	pH
1	0	5	/	50	0.8
2	5	2	2/5	50	0.8
3	5	3	3/5	50	0.8
4	5	4	4/5	50	0.8
4	5	5	5/5	50	0.8
6	5	6	6/5	50	0.8
7	5	7	7/5	50	0.8

Influence of the stability of the arsenomolybdate blue

The experiments were carried out in the 50ml-volumetric flask containing the As(V) solution of 5 mL (2mg/L) and CR solution of 3 ml, pH= 0.8.The absorbance of the arsenomlybdate blue were measured during the time from 0 tho 120 min.

RESULTS AND DISCUSSION

The factors influence on the arsinization process

The factors influencing on the arsinization were determined by the absorbance measurement of the arsenomolybdate blue complex in the following cases.

The dependence of absorbance on V_{HCl}

The dependence of absorbance of the arsenomolydate blue on V_{HCl} is presented in the Fig. 1.

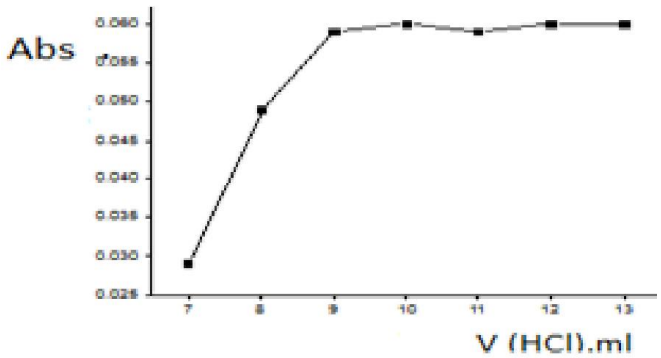

Fig. 1. The dependence of absorbance on V_{HCl} volume (or pH)

The obtained results from Fig 3 indicate that the absorbance of sample increases with the HCl - amount increasing and reaches to a constant value. The increase of absorbance with the varying pH is due to the formation of arsine amount increased. The H^+ role can be explained by the following reactions:

$$4\ H_3AsO_4 + BH_4^- + H^+ \rightarrow 4\ H_3AsO_3 + HBO_3 + H_2O,$$

$$4\ H_3AsO_3 + 3\ BH_4^- + 3\ H^+ \rightarrow 4\ AsH_3 + 3HBO_3 + 3H_2O$$

The obtained arsine gas can be oxidized by $AgNO_3$ and H_2O_2 to form As(V) compound then reacts with CR solution to producing arsenomolybdate blue complex. The results from Fig. 1 and from experimental data in Table 1 have indicated that the optimum conditions for the arsinization process are: pH is from 0.65 to 1.14 ratio of V_{HCl}/V_{NaBH4} = 10/15

The dependence of absorbance on the summa of ($HCl+NaBH_4$)

The dependence of absorbance on the summa of V_{HCl}+$NaBH_4$ is presented in the Fig. 4.

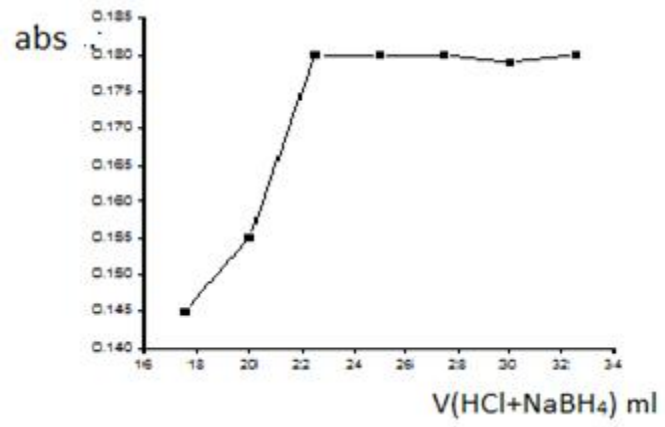

Fig. 2. Dependence of absorbance on V_{HCl}+$NaBH_4$

These experimental results indicate that while the arsenic amount is kept constantly, the absorbance of arsenomolybdate blue complex increases with the V_{HCl}+$NaBH_4$ increasing then reaches to a constant value. The results from Fig.2 and from experimental data in Table 2 have indicated that, in this case the optimum conditions for the arsinization process are:the summa of V_{HCl} + V_{NaBH4} = 25 ml and the ratio of $(n_{HCl}+n_{NaBH4})/n_{As}$ = 23.965/ $2{,}0.10^{-4}$ ~ $1{,}2.10^{5}$, pH = 0.96. These conditions can be applied in practice for producing AsH_3.

The dependence of absorbance on arsenic concentrations

The dependence of absorbance of arsenomolydate blue complex on the arsenic concentrations or volume of arsenic solutions, 0.01mg/L is presented in Fig.3.

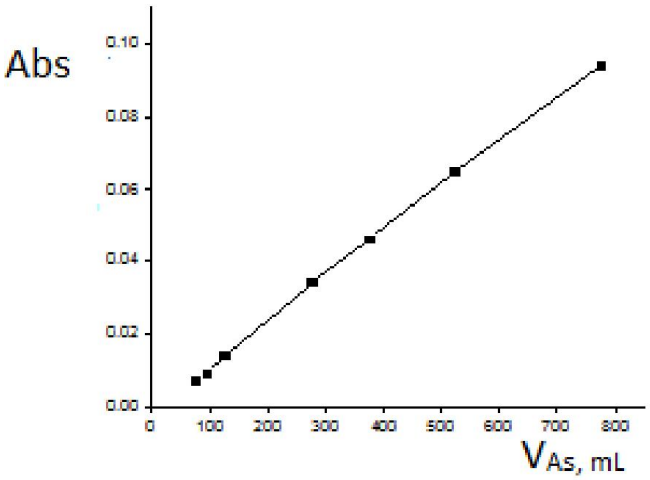

Fig. 3. The dependence of absorbance on the added volume of arsenic solutions

The experimental results indicate that the absorbance of the arsenomolybdate blue complex is proportional to the added arsenic solutions in the range of volume of 50 to 750 ml (0.01mg/L) or from arsenic concentrations of 6.66×10^{-3} to 9.67×10^{-3}mg/L respectively. This is a good base for establishing the standard plot for the arsenic determination.

The dependence of absorbance on the N_2-blowing time

The dependence of absorbance of the arsenomolydbate blue complex on the N_2-blowing time was presented in Fig.4.

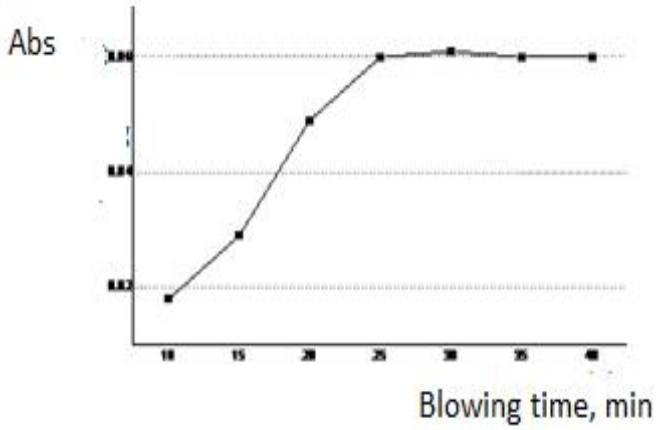

Fig. 4. The dependence of absorbance on the N_2- blowing time

The experimental results have indicated that the sufficient time of N_2-blowing in this case is 30 min.

Results determining the optimum conditions of molybdenum blue formation

The optimum conditions of molybdenum blue formation were determined by the dependence of its absorbance on the pH, ratio of V_{CR}/V_{As} and the stability of arsenomolybdate blue comples for the following cases:

The dependence of absorbance on pH of solution

The results of dependence of absorbence on pH are presented in Fig. 5 via the spectrograma.

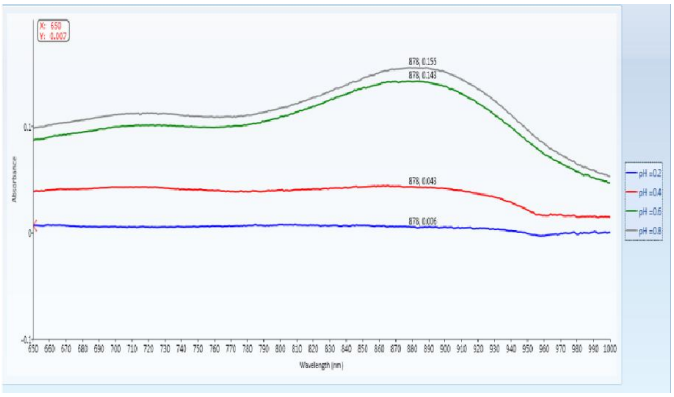

Fig. 5. UV-ViS spectroscopy, sample consisting of 5 mL solution As(V), 2mg/l; 5 ml solution of CR, reaction time of 30 min, pH varying from 0.2 to 0.8.

The results have showed that the pH value of 0.8 can be selected for the experiments as the optimum value.

The dependence of absorbance on the volume of V_{CR}

The experiments were carried out with 5 ml of arsenic solution, 2mg/L; pH= 0.8; the volume of CR solution varying from 2 to 7 mL, reaction time of 30 min. The dependence of absorbance of arsenomolybdate blue on CR volume is presented in Fig. 6.

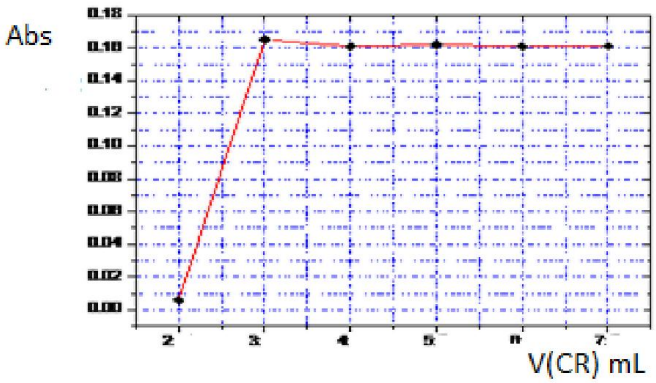

Fig. 6. The dependence of absorbance on volume of CR

The experimental results have showed that the absorbance in the samples increases with volume of CR increased then reached to the constant value when the volume ratio of $V_{CR}/V_{As} \geq 3/5$. In this case the $V_{CR}/V_{As} = 3/5$ is selected as the optimum condition for the experiments.

The stability of arsenomolybdate blue

The results of experiments (not showed here) indicated that the asrenomolybdate blue can be stable for 30min.

The standard plot of the dependence of absorbance asrenomolybdate blue on the As(V) concentration

The standard plot was implemented in the selected optimum conditions is presented in Fig .7.

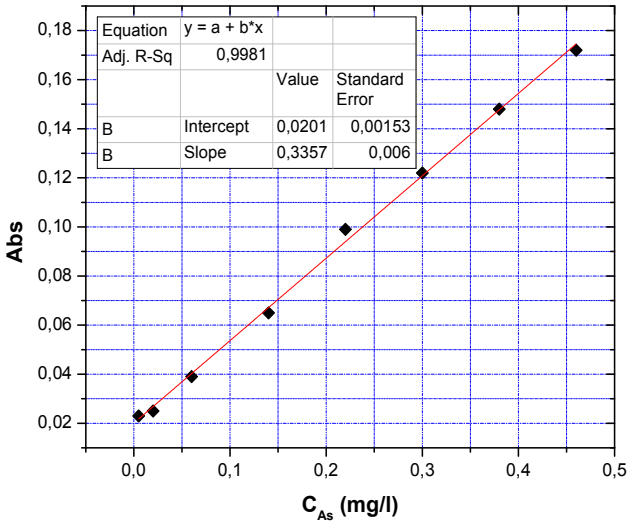

Fig. 7. The standard plot for determintion of arsenic concentration

Basing on the standard plot, the values of LOD (limit of detection) and LOQ (limit of quantification) were determined and are 2ppb, 7ppb respectively

Conclusion

A spectrophotometric method for arsenic determination from water has been studied systematically. The method consists of three steps (i) arsinization producing AsH_3, (ii) $AgNO_3$, H_2O_2 oxidized $AsH_3$to produce As(V), (iii) reaction of As(V) with molybdate and CR reagents to produce molybdenum blue complex. The absorbance of molybdenum blue complex at the wave length of λ = 878nm has been used for arsenic determination. The LOD and LOQ of the method are 2 and 7ppb respectively.

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