

Spectrophotometric Procedure for Fast Reactor Advanced Coolant Manufacture Control

O S Andrienko¹, N B Egorov², I I Zherin² and D V Indyk^{2,*}

¹ V.E. Zuev Institute of Atmospheric Optics 1, Academician Zuev square Tomsk 634055 Russia

² Tomsk Polytechnic University, 634050, Russia, Tomsk, Lenin Avenue, 30

*E-mail: stoya@mail.ru

Abstract. The paper describes a spectrophotometric procedure for fast reactor advanced coolant manufacture control. The molar absorption coefficient of dimethyllead dibromide with dithizone was defined as equal to $68864 \pm 795 \text{ l}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$, limit of detection as equal to $0.0583 \cdot 10^{-6} \text{ g/ml}$. The spectrophotometric procedure application range was found to be equal to 37.88 – 196.3 g. of dimethyllead dibromide in the sample. The procedure was used within the framework of the development of the method of synthesis of the advanced coolant for fast reactors.

1. Introduction

Metal lead enriched by ^{208}Pb is considered to be an advanced coolant for fast reactors by several authors [1,2]. Therefore, there exists a demand in the method for obtaining metal lead enriched by ^{208}Pb isotope from gaseous lead tetramethyl ($\text{Pb}(\text{CH}_3)_4$), which is used as a working media in isotope separation process [2]. The authors [3] show that one of the compounds received after the tetramethyllead bromination is dimethyllead dibromide ($\text{Pb}(\text{CH}_3)_2\text{Br}_2$). While working with the method for obtaining the isotopically enriched lead as the advanced coolant for fast reactors from gaseous lead tetramethyl [4] there appeared a target to control the amount of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ during the $\text{Pb}(\text{CH}_3)_4$ bromination process.

There is a method for spectrophotometric determination of Pb^{2+} , R_3Pb^+ and R_2Pb^{2+} (R – alkyl radical) ions with 4-(2-Pyridylazo) resorcinol known [5]. The use of this method is complicated since no value of molar absorption coefficient of the ions under consideration is represented.

A procedure for spectrophotometric determination of Pb^{2+} , $\text{Pb}(\text{C}_2\text{H}_5)_2^{2+}$, $\text{Pb}(\text{C}_2\text{H}_5)_3^+$ ions is also known [6]. The direct application of this procedure is impossible since no value of molar absorption coefficient of the investigated ions is represented, and the ions under study are different from the ion yielded after the reaction between dithizone and $\text{Pb}(\text{CH}_3)_2\text{Br}_2$.

So, there is no data related to the procedure of the determination of the amount of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ in literature.

The aim of the work is to develop a spectrophotometric procedure for determination of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$.



2. Experimental

2.1. Reagents and equipment

The quality grade of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ (Siberian Chemical Plant, Russia), dithizone (Sigma-Aldrich, Switzerland), CCl_4 (Reachem, Russia), ammonia (Reachem, Russia), sodium sulfite (Reachem, Russia), was for analytical purpose. The quality grade of ammonia citrate (Reachem, Russia), bromine (Reachem, Russia) was synthesis reagents. The buffer solution #1 was prepared according to procedure [7], buffer solution #2 was prepared according to procedure [6]. Spectrophotometer “Thermal visio Evolution 600” (Thermo Scientific, USA) was used in the work.

2.2. Procedure

To prepare a standard solution, 5 ml of 33% of water solution of ammonia citrate, 50 ml. of buffer solution #1 and a weighted before sample containing $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ was put into 500 ml. measuring flask and was mixed until all the components were dissolved. Then, the solution in the flask was diluted with water up to 500 ml. To prepare the dithizone solution, 60 mg. of dithizone were dissolved in 1 liter of CCl_4 . 15 ml. of buffer solution #2 were put into 50 ml. glass reactor, then, an aliquot of standard solution was added. The extraction was carried out for 130 minutes with agitation. After the extraction the organic phase was separated with the help of a funnel and gathered in a 25 ml. flask. The solution in the flask was diluted with CCl_4 up to 25 ml. and was shaken. Spectrophotometric determination of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ ran in the 10.02 mm. quartz cell in comparison with CCl_4 between $350 \cdot 10^{-9}$ and $650 \cdot 10^{-9}$ m.

3. Discussion

Figure 1 represents the absorption curve of dithizone and $\text{Pb}(\text{CH}_3)_2\text{Br}_2$.

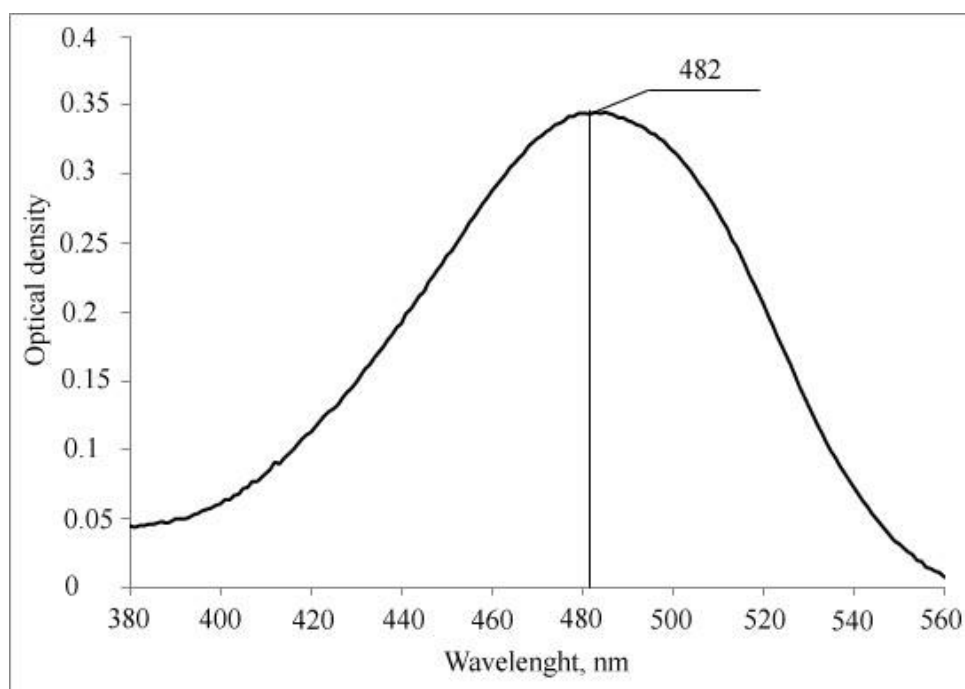


Figure1. The adsorption curve of the complex of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ with dithizone.

The curve shows that complex of dithizone and $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ represents absorption maximum at 482 nm.

Figure 2 reflects the dependence between the optical density and concentration of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ in the sample.

To decrease the influence of random error on the result, each measurement was repeated 5 times. Based on the data represented at figure 2 it may be concluded that Beer's law is kept within the range of concentration of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ equal to 1.5 – 7.9 mg/l of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ that is equal to 37.88 – 196.3 g. of dimethyllead dibromide in the sample. The linearization line equation is $A = 0.1704 \times C(\text{Pb}(\text{CH}_3)_2\text{Br}_2) + 0.0119$ ($R^2 = 0.9992$).

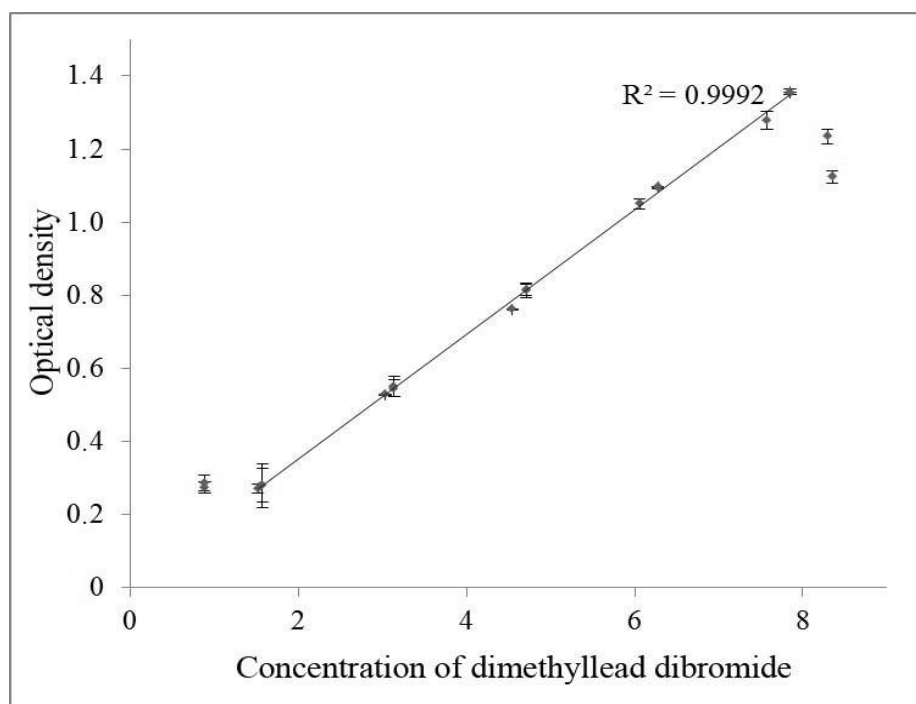


Figure 2. Dependence between the optical density and concentration of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$.

Three standard solutions with measured concentration of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ were prepared to calculate the average molar absorption coefficient of dimethyllead dibromide with dithizone. Then, the concentration of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ was measured by means of the developed procedure. The results are represented in table 1.

Table 1. ϵ $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ calculation data

| Mass of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$, $\text{g} \cdot 10^{-6}$ | D | l, cm | ϵ | $\bar{\epsilon}$ | ω , % |
|--|-------|-------|------------|------------------|--------------|
| 35.6 | 0.267 | 1.002 | 68589 | 68344 | 0.4 |
| 71.2 | 0.536 | | 68889 | | 0.8 |
| 106.8 | 0.801 | | 68675 | | 0.5 |
| 142.4 | 1.063 | | 68375 | | 0.0 |
| 178 | 1.332 | | 68538 | | 0.3 |
| 35.72 | 0.266 | | 68188 | | 0.2 |
| 71.44 | 0.534 | | 68444 | | 0.1 |
| 107.16 | 0.807 | | 68986 | | 0.9 |
| 142.88 | 1.065 | | 68231 | | 0.2 |
| 178.6 | 1.334 | | 68410 | | 0.1 |
| 37.32 | 0.283 | | 69518 | | 1.7 |

| | | | |
|--------|-------|-------|-----|
| 74.64 | 0.552 | 67759 | 0.9 |
| 111.96 | 0.825 | 67446 | 1.3 |
| 149.28 | 1.094 | 67084 | 1.8 |
| 186.6 | 1.386 | 68029 | 0.5 |

The average molar absorption coefficient of dimethyllead dibromide with dithizone was defined with the help of statistical methods and was found to be equal to $68864 \pm 795 \text{ l}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$, relative measurement error did not exceed 1.8% for each of the measurements. The detection limit of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$, calculated with the use of the 3s - criterion ($P = 0.95$, $n = 10$) was found to be equal to $0.0583 \cdot 10^{-6} \text{ g/ml}$. To calculate the within-laboratory divergence, the Kohren criterion was calculated and was found to be equal to 0.3551 which is less than the tabulated point ($S_{\text{tabulated}} = 0.6838$; $P = 0.95$; $f = 3$, $n=5$). This means that the measured results are reproducible.

Five control specimens with known concentration of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ were prepared to verify the results. The concentration of $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ in each sample was measured by means of the developed procedure. The results are shown in table 2.

Table 2. Results of verification of the procedure ($n = 5$, $P = 0.95$)

| | | $\text{Pb}(\text{CH}_3)_2\text{Br}_2$ | Inserted mg/l | Detected mg/l | % | t^* |
|---------------|---|---------------------------------------|---------------|---------------|------|-------|
| Sample number | 1 | 39.2 | 38.58 | 1.58 | 1.78 | |
| | 2 | 78.4 | 77.56 | 1.07 | 1.54 | |
| | 3 | 117.6 | 115.84 | 1.5 | 2.53 | |
| | 4 | 156.8 | 158.16 | 0.87 | 2.29 | |
| | 5 | 196 | 195.26 | 0.38 | 0.67 | |

It may be noted that the relative error is small (not more than 1.58 %) within the range of concentrations to which the procedure can be applied. Some deviations of the results between the known and measured concentration may be connected with a random error, since the value of calculated Student's coefficient (t^*) is less than the tabulated point ($t^* = 2.78$; $n = 5$; $P = 0.95$).

4. Conclusion

A spectrophotometric procedure for the determination of dimethyllead dibromide during the manufacture of fast reactor advanced coolant has been developed. The molar absorption coefficient of dimethyllead dibromide with dithizone was found to be equal to $68864 \pm 795 \text{ l}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$, the limit of detection was equal to $0.0583 \cdot 10^{-6} \text{ g/ml}$. The range of use of the spectrophotometric procedure was found to be equal to 37.88 – 196.3 g. of dimethyllead dibromide in the sample. Relative error within the range of application of the procedure didn't exceed 1.58 %.

Reference

- [1] Khorasanov G L, Blohin A I and Valter A.A 2012 *Nuclear Reactors* Amir Zacarias (InTech) 57
- [2] Khorasanov G L et al 2013 *Application of stable lead isotope Pb-208 in nuclear power engineering and it's acquisition techniques* (NY: Nova publishers)
- [3] Akimov D V, Andrienko O S, Egorov N B, Zherin I I, Indyk D V, Kazaryan M A and Obmuch K V 2013 *J. For Alternative En. and Ecol.* **4/1** 77

- [4] Andrienko O S, Afanasyev V G, Egorov N B, Zherin I I, Indyk D V, Kazaryan M A, Poleshuk O H and Sokovikov V G 2011 Method for obtaining metal lead *Patent RUS #2415185*
- [5] Schmidt U, Huber F 1978 *Analytica Chimica Acta* **98** 147
- [6] Henderson S R and Snyder L J 1961 *J Anal. Chem.* **33/9** 1172
- [7] Shvarcenbah G and Flashka G 1970 *Chelatometric Titration* (Moscow: Chemistry)