

ATTEMPTS FOR QUANTITATIVE DETERMINATION OF Pb^{2+} BY UTILIZATION OF SEDIMENTARY CHROMATOGRAPHIC COLUMN

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Lead cations are encountered in a variety of materials: ores, metals, alloys, nutritive substances, concrements etc. A great number of methods are known for qualitative identification and quantitative determination of Pb^{2+} . With discovering of the chromatographic methods, new possibilities were created for Pb^{2+} assaying in a given material for investigation. Lately, the ionmetabolite resins find a particular field of application in analytical chemistry. Thus for Pb^{2+} determination *F. Nelson* and *K. Kraus* (13) utilize anionite doux — 1, and *I. Morachevski* and assoc. — anionites PE-10 and EDE-10 (13). For proving lead traces in nutritive products *K. Streat* and *G. Siborg* (13) have elaborated a feasible method utilizing the amberlite JRA-400.

Sedimentary chromatography on adequate column also provides a number of possibilities for determination of various cations and more particularly Pb^{2+} .

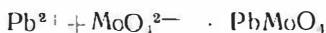
E. N. Gapon and *I. M. Belenkaya* (2) suggest a sedimentary chromatographic method for qualitative determination of Pb^{2+} in mixture with other cations with the utilization of sedimentary column from silicagel. *A. I. Komlev* and *L. I. Tzimbalista* (14) have elaborated a semimicrochromatographic method for determination of cations on columns of quartz, asbestos etc.

An interesting method for establishing the ions of Al^{3+} , Fe^{3+} , CO^{2+} , Cu^{2+} and Pb^{2+} has been devised by *F. M. Shemiakin* and *B. F. Chapigin* (12), utilizing sedimentary and partition chromatography.

E. N. Gapon and *G. M. Shuvaeva* have obtained sedimentary chromatograms of the Ag^+ , Pb^{2+} , Hg^{2+} and Bi^{3+} cations by using base Al_2O_3 as a carrier and iodide as sedimentator (7). A method has been suggested by *K. M. Olshanova* and *V. D. Kopilova* (7) for Pb and Hg assessment on sedimentary chromatographic column with carrier base Al_2O_3 and sedimentator $K_2Cr_2O_7$. They point out that sedimentary chromatographic methods could be successfully employed for quantitative determination of the ions indicated.

With a view to testing new possibilities for quantitative determination of Pb^{2+} , we attempted the isolation of Pb^{2+} from a sample solution of Pb $(NO_3)_2$ on a column with base Al_2O_3 as carrier and Na_2SO_4 as sedimentator. Thereupon the problem was to eluate Pb^{2+} from the column, where they are found as $PbSO_4$, and their titration in the solution. As a result of repeated research studies, the sodium acetate solution, alkalized with ammonia proved to be most suitable for eluation. In the solution Pb^{2+} are determined

titrimetrically with $(\text{NH}_4)_2\text{MoO}_4$ according to the *Feinberg* method (11) with appropriate indicator:



The possibility was investigated for Pb^{2+} isolation from a solution containing Cu^{2+} , Cd^{2+} , Fe^{3+} , Al^{3+} and Mg^{2+} , as well as for the repeated utilization of the same column.

Materials

The sample solution of lead cations, containing 0,0345 mg/ml Pb^{2+} , established iodometrically after *N. P. Penchev* and *B. N. Zagorchev* (8), chromatographic columns with filling — base Al_2O_3 and Na_2SO_4 in ratio 5 : 1 with height of filling 200 mm and diameter of the column 10 mm; 15% solution of CH_3COONa , alkalized with 10% ammonia; solution of ammonia molybdate, whose concentration is computed on the basis of a formula and 1 ml equivalent to 0,657 mg Pb^{2+} ; stannic rodanate indicator, containing 2,5 gr stannic bichloride, 2,5 gr ammonia sulphodianide and 10 ml water. The latter must be freshly prepared in 95% ethanol.

Method

The carrier base Al_2O_3 for chromatographic purposes and the sedimentator Na_2SO_4 are mixed up in dry environment, proportion 5 : 1 and tritiated till fine powder is obtained. As column a glass tube is used with diameter 10 mm. A common buret could be utilized for the same purpose. At the lower end of the column about 10 mm glass cotton is placed for retaining the filling. The latter is poured in compact (compressed) state reaching a height of about 20 mm. Above the filling about 10 mm glass cotton is also placed. Next the column is mounted on a vacuum bottle furnished with a water pump. A predetermined volume of sample solution (50 ml) is passed through the column at a rate amounting to about 24 drops per minute, which is secured and controlled by means of the vacuum created by the water pump. Following the complete aspiration of the sample solution, the precipitated Pb^{2+} are eluted with 20 ml 15% solution CH_3COONa , alkalized with 10% ammonia. Previous to repeated employment of the columns, they are washed up with 10 ml 95% ethanol.

The Pb^{2+} titration is carried out slowly by means of microburet with solution of ammonia molybdate with known concentration, under continuous shaking and with external stannic-rodanide indicator. The equivalent point is established at the appearance of faintly rose staining following dripping of a drop of the indicator over a drop of the solution investigated, transferred over a filter paper. During titration the rosy colouring remains unaltered. In order to control the degree of Pb^{2+} retaining in the column, their concentration was determined in the sample solution passed. Previous to titration 10 ml 15% CH_3COONa is added to the solution. Analogous control was performed also after eluation as well.

Sample solutions were tested with concentrations lower than 0,01 mg/ml Pb^{2+} . With them Pb^{2+} retaining in the column is unsatisfactory, due to the

solubility of $PbSO_4$. In concentrations above 0,05 mg/ml other methods are also suitable for the purpose — determination. Besides with pure sample solution of lead nitrate, experiments were carried out with solutions containing in addition to Pb^{2+} , also ions of Cu^{2+} , Cd^{2+} , Fe^{3+} , Al^{3+} and Mg^{2+} . The latter do not interfere with retaining and elution of Pb^{2+} .

Results

The results of the investigations performed are illustrated in tables 1 and 2.

Table

Pb^{2+} content in mg/ml in sample solutions, containing other cations as well

Sample solution of Pb^{2+} containing Cu^{2+} , Cd^{2+} , Fe^{3+} , Al^{3+} and Mg^{2+}			Pb^{2+} before elution	Pb^{2+} after elution	Loss after elution
Pb^{2+} obtained	Pb^{2+} determined				
	iodometrically	by weighing			
0.033	0.0349	0.0345			
1			0.001329	0.03274	0.0018
2			0.001435	0.03275	0.0017
3			0.001403	0.03275	0.0018
4			0.001330	0.03207	0.0014
5			0.001401	0.03300	0.0015
6			0.001348	0.03261	0.0019
7			0.001314	0.03311	0.0014
8			0.001720	0.03196	0.0026
9			0.001478	0.03269	0.0018
10			0.001314	0.03311	0.0014
11			0.001324	0.03312	0.0014
12			0.001450	0.03282	0.0017
Mean arithmetical			0.001366	0.03278	0.0017
Mean square deviation			$\pm 3.1 \cdot 10^{-6}$	$\pm 9 \cdot 10^{-7}$	$\pm 9.8 \cdot 10^{-7}$
Mean arithmetical			$\pm 0.884 \cdot 10^{-6}$	$\pm 2.5 \cdot 10^{-7}$	$\pm 2.7 \cdot 10^{-7}$
Probability — 0.001			4.444	4.44	4.44

Discussion

Obviously the method could be applied for investigating solutions with slight Pb^{2+} concentrations, of the order 0,05—0,01 mg/ml.

The losses previous to elution are as follows:

during single utilization of the columns	4,74%
during twofold utilization of the columns	20,35%
during triple utilization of the columns	45,85%

Results content of Pb^{2+} in mg/ml

[illegible]

which is an indication that the single use of the columns is really expedient. Analogous results are obtained also after assessment of the losses following elution, namely:

with single utilisation of the column	8,40%
with twofold " " " "	30,14%
with threefold " " " "	36,72%

Titration of samples couldn't be carried out with a more diluted molybdene solution of the one stated above, due to the insensitivity of the indicator in stronger dilutions.

Conclusion

The method proposed by us is suitable for Pb^{2+} separation of a mixture and their quantitative determination. The single use of the columns is recommended.

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ОПЫТЫ КОЛИЧЕСТВЕННОГО ОПРЕДЕЛЕНИЯ Pb^{2+} ПРИ ИСПОЛЬЗОВАНИИ ОСАДОЧНОЙ ХРОМАТОГРАФИЧЕСКОЙ КОЛОННЫ

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Р Е З Ю М Е

Описывается количественное определение Pb^{2+} при использовании осадочной хроматографической колонны. Наполнение колонны состоит из базисного Al_2O_3 как носителя и Na_2SO_4 как осадитель в соотношении 5 : 1. Элюирование $PbSO_4$ из колонны производят 15% CH_3COONa алкализованным (10% аммиаком). Титруют Pb^{2+} в растворе раствором аммониевого молибдата известной концентрации в присутствии наружного медно-роданидного индикатора. Наличие в исследуемом растворе Cu^{2+} , Cd^{2+} , Fe^{3+} , Al^{3+} и Mg^{2+} не мешает определению. Как наиболее подходящую концентрацию для точного определения Pb^{2+} указывается 0,05—0,01 мг/мл. Многократное использование одной и той же осадочной колонны не рекомендуется.