Determination of Zinc and Lead by Means of Sodium Diethyldithiocarbamate

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Introduction

Sodium diethyldithiocarbamate was introduced by Delepine⁽¹⁾ as a reagent for copper. Subsequently Callan and Henderson⁽²⁾ also pointed out the sensitivity of this reagent for copper.⁽³⁾ Then the reagent has been used for the determination of a minute amount of copper.⁽³⁾ The author⁽⁴⁾ also showed in testing this method that it reacts most sensitively with copper among many other metals giving white turbidity or coloration and he improved the method by the extraction with carbon tetrachloride in the presence of hydroxylamine with the result of increasing the accuracy and sensitivity of the determination.

In 1935 Atkins,⁽⁵⁾ while testing copper with this reagent, found that a dense turbidity produced immediately on addition of the reagent to the sample of water taken from a well. He concluded that it was due to the presence of zinc and was quite an unexpected phenomenon. He has given a brief description of the determination of zinc using the Nessler tube and showed that it is as delicate as the ferrocyanide method and superior to the colorimetric method by resorcinol. Then Miller⁽⁶⁾ determined zinc in a sample of water in the same manner with fairly good results. In connection with the study on the colorimetric determination of copper with this reagent, the reaction of zinc and lead were also studied by the author. Thus a possible application for the turbidimetric determination of both of these elements is described in this report.

Experiment

A. Reaction of Zinc

a. Effect of *p*H on the Turbidity.—The influence of the acid concentration on the turbidity is evident. The influence was tested on various *p*H values and it was found that maximum turbidity is obtainable at *p*H 4.8 (Table 1). To make the turbidity maximum, the comparison must be made letting the solution stand for half an hour after the reagent has been added.

The change in turbidity on standing was tested as shown in Table 2.

Table 1

*p*H	Turbidity	(Extinction	coefficient)
	I	II	III
3.8	0.205	—	—
4.8	0.242	0.173	0.456
6.2	0.219	—	0.402
6.8	0.184	0.149	0.395
7.9	0.154	—	0.376
9.8	—	0.105	0.237
11.0	—	0.037	—
11.8	—	0.025	0.029

Table 2

A. The Relation between the Change in Turbidity and Time

Time, min.	5	10	20	30	60	120	150
*p*H 4.8	0.125	0.156	0.170	0.173	0.174	0.176	0.171
*p*H 6.2	0.328	0.380	0.380	0.382	0.387	—	—
*p*H 8.8	0.091	0.100	0.119	0.118	0.118	0.120	—

B. The Change in Turbidity after 24 Hours

*p*H	Turbidity (Extinction coefficient)	
	after 30 min.	after 24 hrs.
2.8	0.103	0.091
4.8	0.186	0.149
6.6	0.159	0.148
8.9	0.121	0.080

The turbidity seems to diminish on standing even at a suitable *p*H, but in practical use this has no serious effect as the determination will

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(1) M. Delepine, *Bull. Soc. Chim.*, (4) **3**, 652 (1908); *Compt. rend.*, **146**, 981 (1908).

(2) T. Callan and J. A. Henderson, *Analyst*, **54**, 650 (1929).

(3) D. L. Drabkin and C. S. Waggoner, *J. Biol. Chem.*, **89**, 51 (1903); C. A. Elvehjem and E. A. Hart, *J. Boil. Chem.*, **91**, 37 (1931); L. A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932); McFarlane, *Biochem. J.*, **26**, 1022 (1932); N.D. Sylvester and L. H. Lampitt, *Analyst*, **60**, 377 (1935); L. W. Conn *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 15 (1935); F. Nydahl, *Z. anal. Chem.*, **116**, 315 (1939).

(4) Y. Murakami, *Bull. Chem. Soc. Japan*, **22**, 3 (1950).

(5) W. R. G. Atkins, *Analyst*, **60**, 400 (1935).

(6) C. F. Miller, *Chemist-Analyst*, **20**, 8 (1931).

be made before any change occurs, and then any stabilizing agent is not required for it. The higher the *p*H value of the solution is the less remarkably the turbidity is formed. Therefore no turbidity occurs if the solution is made alkaline with a slight excess of ammonia. The turbidity once formed is easily diminished in the same way and the solution becomes perfectly clear on standing for five minutes.

From these experiments it may be concluded that the solution should be buffered at *p*H 4.8 with 12.17 ml. of 0.1 *N* acetic acid and 7.83 ml. of 0.1 *N* ammonia; the turbidity comparison is preferably performed in half an hour after the reagent is added.

b. Temperature and Turbidity.—A number of experiments were carried out at various temperatures in a thermostat to seek the relation between turbidity and temperature of the solution (Table 3).

Table 3

Temperature and Turbidity (at *p*H 4.8)

Temp. °C.,		10	15	20	25
Turbidity (Extinction coeff.)	I	0.149	0.305	0.360	0.268
	II	0.147	—	0.347	0.238

The results of these experiments indicated that 20° is most favorable for obtaining maximum and stable turbidity.

c. Application of Lambert-Beer's Law.—It has not been known whether the reaction of zinc with the reagent conforms with the Lambert-Beer's law or not, but the author has found it sufficiently conforms with the law if turbidity is produced closely following the conditions recommended above.

Thus the following results were obtained when 10 ml. of 0.1% solution of the reagent is added to the solution to be tested, buffered at *p*H 4.8 as described above (Table 4).

Table 4

Zinc, γ in 50 ml.	20	40	80	100
Extinction coeff.	0.181	0.358	0.716	0.910
E_r (calculated)	0.0905	0.0895	0.0895	0.0910

The comparison is made with Pulfrich photometer using S 43 (434 mμ) filter after the solution being made up to 50 ml.

d. Reaction of Other Ions.—The reagent is not specific to copper alone but similarly reactive with many other metals. For details of interference, references may be made to the reports of Callan *et al.*(2) and the author(4) besides those given below. These interferences, however, were rarely encountered in determining zinc in natural water as well as other water samples. Alkali and alkaline earth metals do not react with it, thus making it superior to the resorcinol method. It is most sensitively reactive with copper. Its sensitivity to some metals can be compared by calculating E_r from the results, which means the extinction coefficient of 1 mm. thickness of the solution containing 1 γ of the element in question in 1 ml. If a considerable amount of iron is present, as is usually the case, a dirty yellow coloration is produced though the sensitivity to iron is much lower than that to the element in question. But it is desirable to prevent the reaction of iron. This is usually performed by removing iron as hydroxide as in the copper determimation recommended by Callan and Henderson.(2) Haddock *et al.*(3) recommended the removal of iron as hydroxide precipitate. However, a considerable amount of zinc is carried down with iron hydroxide though a part of it may also be expected to pass into the filtrate owing to the formation of $Zn(NH_3)_4^{\cdot\cdot}$. Therefore it becomes desirable to prevent the reaction of iron with the other method.

Elvehjem *et al.*(3) described a method of preventing the precipitation of iron by the addition of citrate and the successive addition of 1% gum arabic solution. McFarlane proposed the use of sodium pyrophosphate for the same purpose. The latter is preferable to the former as the *p*H of the solution recommended is much nearer to the most suitable *p*H value than in the former method, though the sensitivity is somewhat decreased. Naturally in this case a standard curve at this *p*H value should be constructed. Manganese interferes to a considerable extent by imparting a pinkish color to the solution which is an indication of the oxidation of manganese by the air in the solution. However, this coloration is unstable and the solution soon becomes virtually colorless, provided that only a small amount of manganese is present. Pyrophosphate also reduces the coloration.

The interferences of nickel, cobalt and bismuth which are the chief interfering metals in this reaction are rarely encountered because of their rarity in natural waters. The presence of cyanide prevents turbidity but citrate does not interfere even if a considerable amount may be present.

B. Reaction of Lead

The author has determined copper in

biological matters with the reagent after separating lead, zinc and copper from the sample by dithizone and isolating copper from the others by treating it with 0.01 *N* hydrochloric acid.(4) In this procedure copper remains as dithizonate but zinc and lead are transferred into the hydrochloric acid solution as chlorides. From this point, some attempts were made to the simultaneous determination of the latter two in an aliquot portion of the sample. There exists a more sensitive colorimetric determination after separating both of these elements. However, the turbidimetric determination with the reagent finds some important uses as well.

Tompsett and Anderson(7) described a method of preliminary separation of lead in excreta and in tissue by this reagent and concluded that it is the most suitable reagent for this purpose as such. A preliminary separation is absolutely required with a sample of a high iron content. Then Tompsett determined lead in potable water in the same way and showed that there are several distinct advantages, e.g., more stable turbidity not affected by oxidant and easy extractability with ether.

A white turbidity is produced by the presence of lead and a perceptible turbidity is observed when the reagent is added to 0.05 mg. of lead in 100 ml. aqueous solution. It was found for the first time by the author that a white turbidity due to lead also conforms with the Lambert-Beer's law as shown in the Table 5.

Table 5

Conformity to the Law

Pb (γ in 50 ml.)		100	200	300
Extinction coefficient	I	0.268	0.532	0.812
	II	0.261	0.541	0.841
E_r (calculated)		0.0264	0.0268	0.0275

Table 6

Reproducibility in Determining Lead

Expt.	Extinction coefficient	Pb (γ in 50 ml.)
I	0.122	46
	0.124	47
	0.121	46
II	0.335	128
	0.337	128
	0.340	130
III	0.409	157
	0.411	158
	0.422	161

Evidently the presence of lead interferes the determination of zinc with the reagent. However, a preliminary separation can be successfully made with dithizone in the presence of potassium thiocyanate as recommended by Hibbard or by other appropriate methods.(8)

The author also tested the possibility of the determination of zinc without a preliminary separation from lead. A white turbidity due to lead is not affected by a slight excess of ammonia, while that due to zinc is thoroughly diminished. Some attempts were made to use this remarkable difference. Thereupon the total turbidity first, and the remaining turbidity afterwards, are measured in the same aliquot portion after the turbidity due to zinc is diminished by the addition of 8 ml. of saturated ammonia and 2 ml. of 1 *N* potassium hydroxide.

Table 7

Reproducibility in Determining Zinc

Expt.*	Extinction coefficient	Zn (γ in 50 ml.)
I	0.115	13.0
	0.124	14.0
	0.123	14.0
II	0.177	19.6
	0.168	18.8
	0.168	18.7
III	0.682	76.0
	0.683	76.0
	0.670	75.0

* *p*H 4.8 ta 20°, 30 mm. cell used.

The subtraction of the latter reading from the total will give the experimental value for zinc but it is definitely higher than the true value though the reasons are not yet known. Therefore zinc should be determined from the standard curve thus obtained.

From these results it can be concluded that for a rapid determination of zinc in the presence of lead when speediness is essential and accuracy less questioned, this turbidity subtraction method is found most suitable. Even in this case lead can be directly determined with a good result from the latter reading. Thus it was found that a minute amount of zinc less than 40 γ in 50 ml. is permissible in the determination of lead when it is less than 100 γ.

Method

In the absence of the interfering elements

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(7) S. L. Tompsett and A. B. Anderson, *Biochem. J.*, **29**, 1851 (1935); *Analyst*, **60**, 772 (1935); S. L. Tompsett, *Analyst*, **61**, 591 (1936).

(8) E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **9**, 464 (1937); P. L. Hibbard, *ibid.*, **9**, 127 (1937); N. D. Sylvester and E. B. Hughes, *Analyst*, **61** 734 (1936).

described above, zinc may be turbidimetrically determined as follows : the solution to be tested is buffered at pH 4.8 with 7.83 ml. of 0.1 N ammonia and 12.17 ml. of 0.1 N acetic acid and is kept at 20° after diluted to about 40 ml. Then add 10 ml. of 1% sodium diethyldithiocarbamate solution and make up to a final volume of 50 ml. The turbidity is measured with the Pulfurich photometer using S 43 (434 mμ) filter after 30 minutes. Zinc can be determined with the following accuracy (Table 8).

Table 8

Accuracy in Determining Zinc in Standard Solution

Extinction coefficient	Found Zn, γ in 50 ml.	Present Zn, γ in 50 ml.	Difference, γ
0.177	19.6	20.0	−0.4
0.176	19.5	20.0	−0.5
0.168	18.8	20.0	−1.2
0.187	21.0	20.0	+1.0
0.362	40.8	40.0	+0.8
0.360	40.4	40.0	+0.4
0.347	38.5	40.0	−1.5
0.734	82.0	80.0	+2.0
0.712	79.7	80.0	−0.3
0.704	78.6	80.0	−1.4

In case lead is present in the solution to be tested and speediness is more essential than accuracy, the determination may be performed by the turbidity subtraction method (Table 9). The total turbidity at pH 4.8 is measured in the same way as described above. Next the remaining turbidity is again measured after the turbidity due to zinc has been eliminated by the addition of 8 ml. of saturated ammonia solution and 2 ml. of 1 N potassium hydroxide solution.

Table 9

Turbidity Subtraction Method

Zn, $\frac{\gamma}{500}$ ml.	Pb, $\frac{\gamma}{500}$ ml.	E (mixed turbidity)	E(due to Pb)	E of Pb (calc.)	Pb (found), γ	Pb (error), γ
25	0	0.289	0.031	—	—	—
25	50	0.543	0.167	0.136	52	+ 2
25	100	0.750	0.339	0.308	118	+18
25	200	0.894	0.591	0.560	214	+14
40	0	0.360	0.016	—	—	—
40	50	0.759	0.161	0.145	53	+ 3
0	100	0.275	0.265	0.249	95	− 5

Zinc is calculated by subtracting the value from the total value using the empirical standard curve previously constructed. Lead is also determined with the standard curve since it conforms with the law in the case where zinc less than 40 γ in 50 ml. is present with 100 γ lead.

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