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COLORIMETRIC ANALYSIS FOR CADMIUM -
DIPHENYLTHIOCARBAZONE (DITHIZONE) METHOD

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ABSTRACT

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The well known colorimetric method for determining cadmium by means of dithizone has been reinvestigated and found applicable to solutions containing interfering ions such as are found in the plant. Copper, however, must be removed prior to using this analytical procedure.

180 1

The colorimetric analysis for cadmium in T metal, T_3O_8 , and TF_4 previously reported in ER 109¹ was investigated to determine if it were quantitative in the presence of the ions commonly present in gunk solutions and the water washes from the ethers used in gunk extractions.

It was found that cadmium can be quantitatively determined² in the presence of TO_2^{++} , Ca^{++} , Al^{+++} , Ri^{++} , Cr^{+++} , Fe^{+++} , Mn^{++} , and $MoO_4^{=}$; however the cupric ion (Cu^{++}) interferes greatly, even when present in small amounts and has to be removed prior to the analysis.

Precipitating the copper as cuprous thiocyanate ($CuSCN$) proved to be rapid and a sufficiently quantitative method. To do this, an aliquot of the sample was diluted to about 100 ml, 10-15 ml sulfurous acid (6% SO_2) was added and after several minutes the copper was precipitated with an excess of ammonium thiocyanate dissolved in a little water. After occasional stirring during a period of about 10 minutes the precipitate can be filtered off and the filtrate diluted to a definite volume from which aliquots for analysis can be removed.

PROCEDURE

1. Dilute the copper free sample taken for analysis to 90 ml and place in a 125 ml separatory funnel.
2. Add 10 ml conc. 50% Ammonium Citrate solution.
3. Add 3-4 drops thymol blue and make solution just basic w: NH_4OH . Then add 5-7 ml conc. NH_4OH excess.
4. Extract by shaking 1 minute with successive 5 ml portions of dithizone I (0.02%) until the CCl_4 layer remains a clear green. Usually, at least 5 extractions are necessary. Combine the CCl_4 extracts and transfer to another 125 ml separatory funnel. Discard aqueous layer.

¹ See also CC-660 and CC-581.

² Large amounts of Cadmium can be determined gravimetrically with 2-mercaptobenzothiazole (See Report C-1365.3). 180 2

5. Wash the extract by shaking with two 20 ml portions of redistilled water, or until the washings remain colorless. Organic layer may be drained into a small beaker between washes.
6. Transfer organic layer to a clean separatory funnel and extract with 10 ml. 0.01N HCl for at least 5 minutes, shaking thoroughly. Discard organic layer even though colored.
7. Wash acid layer by shaking 1 minute with 5 ml portions of dithizone II (0.002%) until the CCl_4 layer remains a clear green. This step removes last traces of copper and nickel. Discard the organic washes.
8. Wash with 1-2 ml portions of reagent CCl_4 until the washings are colorless. Discard these.
9. To the aqueous layer add 5 ml 10% purified ammonium citrate solution, 5 ml 20% NaOH, and then pipette in exactly 10 ml of dithizone II (0.002%). Shake $1\frac{1}{2}$ minutes.
10. Filter the organic layer through a small filter paper directly into an absorption cell. Read at 520 m μ . The optimum range is from 1 to 13 micrograms cadmium.
11. Blanks and reference solutions for the standard curve may be made up by adding the desired micrograms of cadmium to 10 ml 0.01N HCl and proceeding at step #9; however since there is some loss, in accurate work, it is best to prepare the standard curve from solutions that have been put through the entire procedure.

PREPARATION OF SOLUTIONS

AMMONIUM CITRATE (conc - 50%): To 300 g reagent grade citric acid, add conc. NH_4OH with cooling until pH = 4.

AMMONIUM CITRATE (10% purified): Dilute 50 ml to 250 ml with redistilled water. Make slightly basic with NH_4OH and extract with 20 ml portions of DITHIZONE I (.02%) until organic layer remains green. Wash with reagent CCl_4 until

180 3

colorless.

DITHIZONE I (0.02%): Weigh 0.02 g diphenylthiocarbazone into 100 ml reagent CCl_4 . Extract by shaking several minutes with 100 ml redistilled water containing 10 ml conc. NH_4OH . Discard organic layer and any precipitate. Wash aqueous layer with 5 ml portions of reagent CCl_4 until it remains colorless. Make aqueous layer acid (HCl) and extract dithizone with three 30 ml portions of CCl_4 . Dilute dithizone to 100 ml with CCl_4 and store in amber bottle. This solution should be made fresh every 3 days. Prepare in 300 - 500 ml quantities.

DITHIZONE II (0.002%): Dilute above solution 10 times with reagent CCl_4 , store in amber bottle - prepare fresh every day (100 ml). HCl 0.01N in redistilled water.

NaOH 20 gms/100 ml in redistilled water.

The colorimetric determinations were carried out on the Beckman Quartz Spectrophotometer. The absorption readings were made at a wavelength of 520 m μ which as shown by Table I is an experimentally determined maximum in the absorption curve for carbon tetrachloride solutions of cadmium dithizonate. Table II gives the experimentally determined curve for the optical density of cadmium dithizonate as a function of concentration. Table III gives the results of the use of the method for determining known amounts of cadmium in the presence of other impurities. Very good agreement has been obtained using this procedure by two people working independently of each other.

TABLE I

ABSORPTION CURVE (7 x Cd/10 ml. CCl₄) FOR CADMIUM DITHIZONATE

<u>mμ</u>	<u>Optical Density</u>	<u>mμ</u>	<u>Optical Density</u>
440	.088	516	.444
460	.158	520	.448
480	.272	522	.444
490	.340	525	.443
500	.396	530	.430
510	.428	540	.350
515	.441	560	.116

TABLE II

BEER'S LAW CURVE (520 mμ) FOR SOLUTIONS OF CADMIUM DITHIZONATE IN CCl₄*

<u>Micrograms Cd /10 ml CCl₄</u>	<u>Optical Density</u>
2.25	.148
4.5	.293
9.0	.584
10.8	.714
13.5	.848
18.0	1.070

* A graph of this data was used in actual analytical determinations of unknowns.

TABLE III

ANALYSES OF SOLUTIONS OF KNOWN CADMIUM CONCENTRATION BY THE COLORIMETRIC PROCEDURE

Sol'n. I	<u>Impurities</u> (micrograms present)		<u>Cadmium</u> (micrograms)	<u>Cadmium Recovered</u> <u>by Procedure</u> (micrograms)	<u>Recovery</u>
Sol'n. I	15000	T ⁶	4.5	4.2	93%
	* 15000	Cu ⁺⁺			
	250	Cu ⁺⁺			
	250	Al ⁺⁺⁺			
Sol'n. II	15000	T ⁶	4.5	4.1	91%
	* 15000	Cu ⁺⁺			
	250	Cu ⁺⁺			
	250	Al ⁺⁺⁺			
Sol'n. III	1000	Mn ⁺⁺	10.8	11.0	102%
	1000	Cr ⁺⁺⁺			
	1000	Fe ⁺⁺⁺			
	1000	Mn ⁺⁺			
	1000	MoO ₄ ⁼			
Sol'n. IV	1000	Ni ⁺⁺	4.5	4.0	89%
	1000	Cr ⁺⁺⁺			
	1000	Fe ⁺⁺⁺			
	1000	Mn ⁺⁺			
	1000	MoO ₄ ⁼			

* Removed by thiocyanate procedure.

It is concluded therefore, that the colorimetric analysis for cadmium by the dithizone method can be applied to solutions containing all the ions commonly found in gunk. Copper, if present, must be removed prior to analysis. This can be done by precipitation of the copper as CuSCN . The optimum range is from 1 to 13 micrograms cadmium at 520 m μ . The time per analysis is $1\frac{1}{2}$ to 2 hours.

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