

DETERMINATION OF CHROMIUM AND LEAD IN PERIODIC ACID SOLUTION AND DIALDEHYDE STARCH¹

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ABSTRACT

Two existing methods have been improved and adapted for the determination of chromium and lead in either periodic acid oxidant solution or dialdehyde starch. Because a periodic acid solution destroys color-producing reagents by oxidation, a procedure was developed to remove all the periodic acid before analyses were carried out. The intensity of the colors produced by the different reagents was measured in a spectrophotometer. A standard solution of dichromate gave a least-squares slope of 2.02 p.p.m. per absorbance unit with a standard deviation from regression of 0.028. Lead gave a slope of 3.57 p.p.m. per absorbance unit with a standard deviation from regression of 0.048.

Dialdehyde starch is a product of the oxidation of starch by a periodic acid solution (4). The starch is modified by cleavage of the carbon bond between C₂ and C₃ (3), to give two aldehyde groups. During the reaction the selectivity of this oxidation undergoes a change in the presence of chromium (5). Also, the rate of oxidation is influenced by the amount of either chromium or lead that is dissolved in the periodic acid solution (oxidant). Lead contamination in the oxidant arises from the lead anode used in oxidizing the iodic acid to periodic acid, and the chromium contamination comes from stainless-steel equipment if used in the oxidation. The quality of the final dialdehyde starch may be impaired if the content of these metals is too high. The starch was found to contain from 5 to 200 p.p.m. of both metals.

This paper describes the adaptation of two highly sensitive colorimetric methods, described by Scott (6,7), for determining small amounts of chromium and lead present in the oxidant and in dialdehyde starch. Methods for the determination of chromium (1,2,9) with the reagent diphenylcarbazide and the determination of lead (8,10) with diphenylthiocarbazone have been published extensively in the literature. Both of these color reagents are easily destroyed by oxidation; therefore, removal of the periodic acid was necessary. The conventional Nessler tubes described by Scott for measuring the color intensity were replaced by a spectrophotometric procedure. Several methods were tried but either they were not sensitive enough to detect these metal ions in the proper range, or they produced results lacking the required degree of accuracy.

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Materials and Methods

Preparation of Samples for Analysis

Oxidant. In a small porcelain dish approximately 10 g. of the periodic acid oxidant solution is weighed, evaporated to dryness on a steam bath, and ashed in a muffle furnace for 16 hours at 600°C. To the cooled sample, 1 ml. concentrated hydrochloric acid is added, and the dish is heated again on a steam bath for 0.5 hour. After cooling, the dish contents are transferred into a 100-ml. heat-resistant volumetric flask with approximately 50 ml. of distilled water.

Solid sodium peroxide is added until the mixture becomes alkaline (pH 10). The solution is then concentrated to approximately 10 ml. by boiling. The sodium peroxide oxidizes the chromium present to dichromate, and boiling the solution in the presence of alkali decomposes any remaining sodium peroxide. The concentrate may have a cloudy appearance. After cooling, 50 ml. of distilled water and enough hydrochloric acid (1:1) are added to acidify (pH 4) the concentrate, whereupon the cloudiness disappears. The volume is adjusted to 100 ml. with distilled water.

Dialdehyde Starch. Sample preparation is similar to that for the oxidant. Five grams of starch with a known moisture content are weighed into a small porcelain dish, and 2 ml. of concentrated sulfuric acid are added. After careful charring, the sample is ashed carbon-free and processed as described for the oxidant.

Chromium. The reagent solution is prepared by dissolving 100 mg. of diphenylcarbazide in 10 ml. of glacial acetic acid and adding 90 ml. of absolute ethyl alcohol.

A portion of the sample solution containing 10 to 100 γ of chromium is pipetted into a 100-ml. volumetric flask. One milliliter of reagent is added, and the sample is slowly acidified with 2 ml. of concentrated hydrochloric acid. The sample is diluted to 100 ml. with distilled water and mixed thoroughly. The red color produced by the reagent will develop in 10 minutes. A blank must be prepared at the same time as the sample.

A Coleman Universal Spectrophotometer, Model 14, was used to measure color intensity. The instrument has an arrangement for reading by null balance. This method of reading increases the accuracy of the measurement. The colored sample was contained in a Coleman C cuvet, $\frac{3}{4}$ in. o.d. by 4 in. long. These cuvetts require at least 10 ml. of solution.

Lead. Commercial-grade diphenylthiocarbazone (dithizone) is used for the reagent preparation. It is purified by dissolving 1 g. in 50 ml.

of chloroform and extracting the solution three times with 75-ml. portions of 1% ammonium hydroxide. The extracts containing the dithizone are combined and acidified with hydrochloric acid. This compound is extracted with three 20-ml. portions of chloroform and recovered by evaporating the chloroform at a temperature not exceeding 50°C. A solution of 10 mg. of the purified dithizone in 100 ml. chloroform is used for the color reaction.

After a preliminary approximation, a portion of the 100-ml. sample solution containing 2 to 20 γ of lead is pipetted into a 50-ml. glass-stoppered separatory funnel. Ammonium hydroxide (1:1) is added to the funnel to raise the pH of the contents above 10. One milliliter of 5% potassium cyanide solution is added to the funnel, followed by 10 ml. of the dithizone reagent. The funnel is shaken vigorously for 30 seconds, and the layers are allowed to separate. The bottom layer, which contains the red-colored complex of lead, is drawn off, and the color intensity is measured as described for the chromium. A blank is prepared simultaneously with the sample.

Results and Discussion

Measurement of Chromium and Lead. Figure 1 shows the results of the measurement of the absorbances of the colored dichromate and

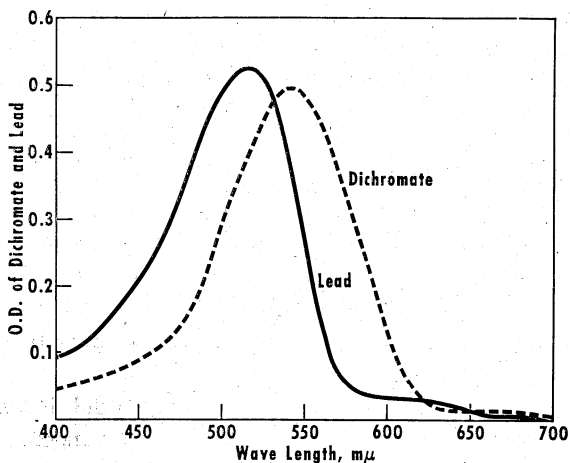


Fig. 1. Adsorption maximum for dichromate (543 $m\mu$) and lead (518 $m\mu$).

lead solutions at wave lengths from 400 to 700 $m\mu$. A peak was observed at 543 $m\mu$ (1) for dichromate and 518 $m\mu$ for lead. These wave lengths were selected for determining standard curves. Standard solutions were prepared from NBS potassium dichromate and CP lead

nitrate. With these, the absorbances of colored solutions containing known concentrations of metal over a range from zero to 1 γ per ml. for dichromate and from zero to 2 γ per ml. for lead were determined. The absorbances were plotted against a concentration and the least-squares slope calculated. For dichromate, the slope was 2.02 p.p.m. per absorbance unit with a standard deviation from regression of 0.028; whereas for lead, the equivalent statistics were 3.57 and 0.048.

The concentration of dichromate ion and lead in the original samples may be calculated by the following equations:

$$\text{Dichromate (wave length 543 m}\mu\text{)} \quad \frac{2.02 \times \text{absorbance} \times 10^4}{W \times A} = \text{p.p.m.}$$

$$\text{Lead (wave length 518 m}\mu\text{)} \quad \frac{3.57 \times \text{absorbance} \times 10^8}{W \times A} = \text{p.p.m.}$$

W = sample weight (starch on m.f.b.).

A = volume in ml. of the portion of the 100 ml. solution used in the color reaction.

Accuracy. The accuracy of both methods was determined by adding given amounts of standard solutions of dichromate and lead to either a freshly prepared periodic acid solution or regular corn starch. The oxidant solution was prepared by dissolving 25 g. of periodic acid in 250 ml. of distilled water and adjusting the pH to 1.8 by adding a saturated solution of sodium hydroxide.

The intercepts of the regression lines of the accuracy data given in Tables I and II did not differ significantly from the origin, so that calculations of slope (b), and standard deviation from regression(s), were made by using this fact. The errors of these data were compared with the error due to the analytical procedure alone as previously noted. To make this comparison, the previously given errors (0.028

TABLE I
DATA OF TESTING ACCURACY OF DICHROMATE METHOD IN OXIDANT
AND DIALDEHYDE STARCH

OXIDANTS (p.p.m. Dichromate)		DIALDEHYDE STARCH (p.p.m. Dichromate)	
Added	Found	Added	Found
24	24	24	22
48	48		
74	76	48	34
98	96	72	68
122	122	244	242
1,316	1,308	732	728
		1,220	1,212
Slope (b)	= 0.994	Slope (b)	= 0.993
Standard deviation from regression(s)	= 0.4	Standard deviation from regression(s)	= 5.8

TABLE II
DATA OF TESTING ACCURACY OF THE LEAD METHOD FOR OXIDANT
AND DIALDEHYDE STARCH

OXIDANTS (p.p.m. Lead)		DIALDEHYDE STARCH (p.p.m. Lead)	
Added	Found	Added	Found
42	42	62	60
82	74	82	78
124	108	104	96
164	164	164	168
206	186	186	174
246	242	206	186
310	282	310	290
370	340	412	386
Slope (b)	= 0.929	Slope (b)	= 0.939
Standard deviation from regression(s)	= 8.1	Standard deviation from regression(s)	= 6.1

and 0.048) in the analytical procedure are multiplied by 200 to give 5.6 for dichromate and 9.6 for lead. The close agreement between these errors and those for the equivalent analyses in Tables I and II indicates that the precision of both analyses is not decreased by the procedure for preparing the samples for analysis. There was, however, a lack of complete recovery of lead, as the slightly low values of the slope for lead indicate. The bias, however, is not great enough to be important to the investigation for which these analyses were developed. Obviously the preparative procedure is adequate for both oxidant and starch samples, and the normally interfering iodate ion has been effectively eliminated.

In the lead analysis, the purity of the reagent dithizone is important. When impure reagent is used, the highly colored blank formed makes analysis impossible. In the chromium analysis, the decomposition of sodium peroxide by boiling before acidification is very important. Failure to accomplish complete decomposition will result in reduction of chromate to chromium ion by acidic hydrogen peroxide and will give an erroneous result.

The best accuracy is achieved when absorbance of the solution is between 0.2 and 0.8. Greater sensitivity can, of course, be obtained by taking larger samples for analysis.

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