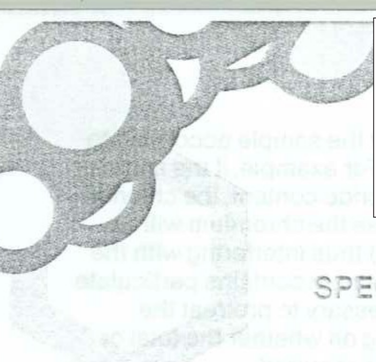
INSTRUMENTS
AT WORK



UV-VIS
SPECTROPHOTOMETRY

The Quantitative Determination of Hexavalent Chromium Using the DMS 90 UV-Visible Spectrophotometer.

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The toxic effects of hexavalent chromium have been known to man for a considerable amount of time (1). Allergies and dermatitis are induced by exposure to hexavalent chromium. Nasal lesions and bronchitis are symptoms shown by chromate workers. The levels of hexavalent chromium both in industrial wastes and the surrounding air must be monitored. Recent studies have shown that chromium compounds could be carcinogenic.

Hexavalent chromium is used extensively in the electroplating industry, tanning and dye works and in photographic processes, and effluents from these industries are now analyzed routinely.

Until recently hexavalent chromium had not been considered to be of any nutritional value. It has been determined that the synthesis of cholesterol and fatty acids is affected by the levels of chromium ions present. Biological samples are also monitored for hexavalent chromium.

The method described in this report determines the dissolved hexavalent chromium content in water. A reddish-purple color is developed when hexavalent chromium is reacted with 1,5-diphenylcarbazide in an acid medium. This can then be measured at 540 nm and an absorbance versus mg Cr curve plotted.

Apparatus

A DMS 90 (Varian P/N 00-100222-01) interfaced with an Apple desktop computer was used in this work. For convenience the Singlecomp Program (Varian P/N 85-100450-00) was used to collect and compile the data into a suitable format. The Scanning Program (Varian P/N 85-100441-00) collected the information required to draw a scan of the chromium peak (Figure 1). Of course, the technique can be used with or without any computer assistance.

The cells used for this experimental work were 50 mm long. The length of the cells could be varied according to the expected level of chromium.

Experimental Procedure

Reagents

Chromium stock solution (1 mL = 0.10 mg)

Dissolve 0.2828 g potassium dichromate ($K_2Cr_2O_7$ — oven dry before use) in distilled water and dilute to 1 litre in a volumetric flask.

Chromium standard solution 1 (1 mL = 0.001 mg)

Dilute 10 mL stock solution to 1 Litre with water.

Diphenylcarbazide Indicator solution

Dissolve 0.25 g of 1,5-diphenylcarbohydrazide in 100 mL of acetone. Store in an amber glass stoppered flask at 4°C. When kept refrigerated, solution will be stable for one week.

Phosphoric acid solution

Dilute 50 mL of concentrated phosphoric acid to one litre with distilled water.

Modifiers

In some cases it may be necessary to use modifiers to stabilize the sample. Use a 4% sodium hydroxide solution to preserve the sample noting the volume added. Also if the sample is known to have a high level of nitrites a few crystals of sulphamic acid can be added to the sample to prevent any possible interference effects.

Procedure

After sample collection treat the sample according to the expected components. For example, if the sample is known to have a high chloride content, the chloride should be removed otherwise the chromium will be bound (as chromyl chloride) thus interfering with the color determination. If the sample contains particulate material then it may be necessary to pretreat the sample or to filter depending on whether the total or the free chromium content is required.

Prepare a series of standards, using chromium standard solution 1, ranging from 0.01 to 0.05 mg chromium (in 100 mL of distilled water). Remember to prepare a blank solution. Note that at least 50 mL is required for analysis. Before the analysis allow the diphenylcarbazide solution to warm to room temperature.

Color development

Pipette a 50.0 mL aliquot of standard or sample to a 125 mL Erlenmeyer flask. To this add 2.0 mL of the diphenylcarbazide indicator solution and swirl to mix thoroughly. Add 1.0 mL of the phosphoric acid solution to the sample and swirl to mix. At this stage the pH of the solution should be less than 2.0. If this is not the case then it will be necessary to add additional acid solution until the pH drops sufficiently. Allow the test solution to stand for 10 minutes to allow for full color development. Figure 2 shows the change in absorbance (color development) against time. Note that while the color is almost fully developed after 5 minutes, the solution should always be left for 10 minutes to ensure consistent results. Transfer the sample to a 50 mm cell and measure at 540 nm.

Prepare a calibration curve either manually or with a computer system such as the DMS 90/PLUS and read the chromium values for the unknown samples. Always prepare a blank solution to allow for any chromium contamination in the reagents.

To calculate the level of hexavalent chromium:

$$\text{Cr(VI), mg/L} = \frac{\text{mg Cr(VI) in sample} - \text{mg Cr(VI) in blank} \times 1000}{V}$$

V = volume of sample used, mL

Results

A series of standards were prepared as described. From these, and using the single component program on the Apple PLUS System a calibration curve was obtained as shown in Figure 3.

Various samples were taken downstream from a tannery works since hexavalent chromium is used in these processes. It was not necessary to pretreat these samples since they were free of particulate matter. Again using the single component program the sample absorbance was computed and the results printed out in a format shown in Figure 4.

A scan of one of the samples showed that the hexavalent chromium peak at 540 nm was broad and quite separate from other peaks (Figure 1). For this reason the slit width used on the spectrophotometer is not as critical as for some other analyses. A slit width of 2 nm was used for this experiment. Figure 4 shows a Cr(VI) content of 0.004 mg in sample 1 and 0.009 mg in sample 2. The procedure was repeated and showed good precision between each set of results.

These results correspond to 40 and 100 µg/L respectively. Results obtained from previous surveys indicated that the levels found in this analysis are in agreement with expected readings (2).

Interferences

The color reaction for the Cr (VI) determination is specific, but various interferences have been reported (3,4). Fe (III), vanadium, molybdenum and mercury have adverse effects on the color development as does nickel in some analytical situations.

Prior to the analysis it is important to oxidize all of the chromium to the Cr(VI) oxidation state if the total chromium content is required. For example, some chromium could be lost if the sample contains a high chloride level since chromyl chloride could be formed.

The sample used for this study was known to contain approximately 200 µg/L iron, lead and zinc. Therefore a chromium standard of 0.01 mg was prepared and spiked with each of these elements in turn to observe if there were any changes due to interferences. As well as mineral interferents two other solutions were prepared to check for any differences. These were 3.5% w/v NaCl and 1.0% $NaNO_2$ respectively.

The results were as follows:

Table 1

Blank	Abs	change from SS (%)
standard solution (SS)	0.378	0.0
SS + 1.0 µg/mL Fe (III)	0.157	− 58.0
SS + 1.0 µg/mL Zn (II)	0.342	− 9.5
SS + 1.0 µg/mL Pb (II)	0.306	− 19.0
SS + 3.5% NaCl	0.389	0.0
SS + 1.0% $NaNO_2$	0.009	− 100

As can be seen from Table 1, the presence of any nitrites interferes with the color determination of chromium. This was overcome by adding in crystals of sulphamic acid according to the expected levels of nitrites. It appears that when Fe (III) is present in the sample, the color formed is an orange-pink instead of the usual red-purple. This is believed to be due to the formation of the iron-diphenylcarbazide complex. Dichloromethane has been used to remove the iron in samples (4). The other elements may also react with the diphenylcarbazide preferentially over chromium, or they could reduce the chromium (VI) to the (IV) oxidation state thereby decreasing the amount of chromium available for analysis.

The expected salt level in seawater samples is about 3%. As seen from the results the addition of salt to the standard solution did not seem to adversely affect the determination of hexavalent chromium.

It is good analytical practice in the preliminary stages of analyzing different samples to carefully match the standards for the major constituents in the sample.

Conclusion

The sensitivity of this colorimetric method enables the analyst to easily determine low levels of chromium. The time required to analyze the samples is minimal and the precision is good. For these reasons the analysis of hexavalent chromium using the diphenyl carbohydrazide is particularly successful for environmental samples.

References

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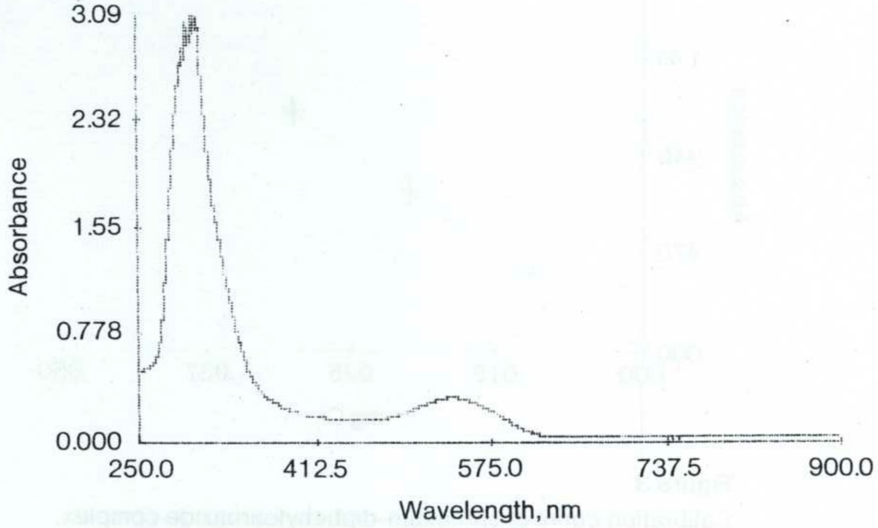

Figure 1

Scan of chromium-diphenylcarbazide complex.

Slit width — 2 nm.

Scan rate — 50 nm/minute.

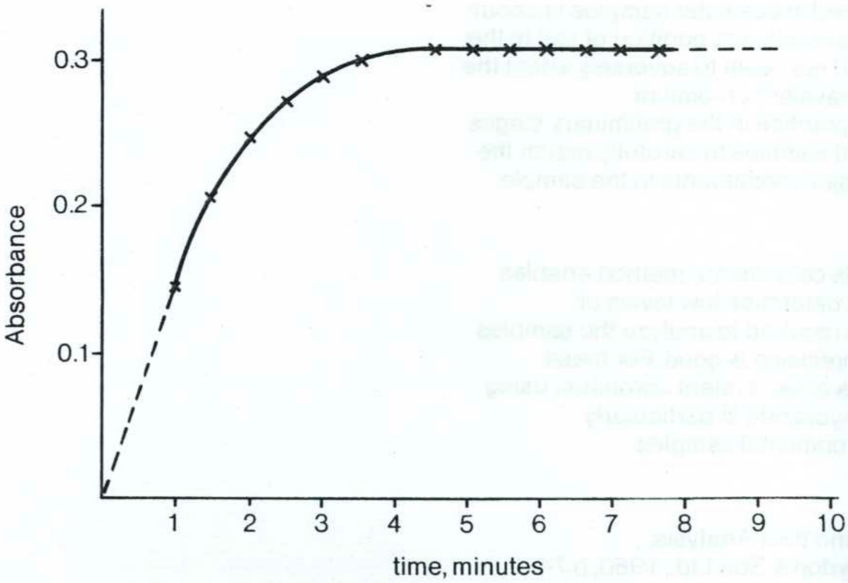

Figure 2

Plot of color development, Absorbance versus time in minutes.

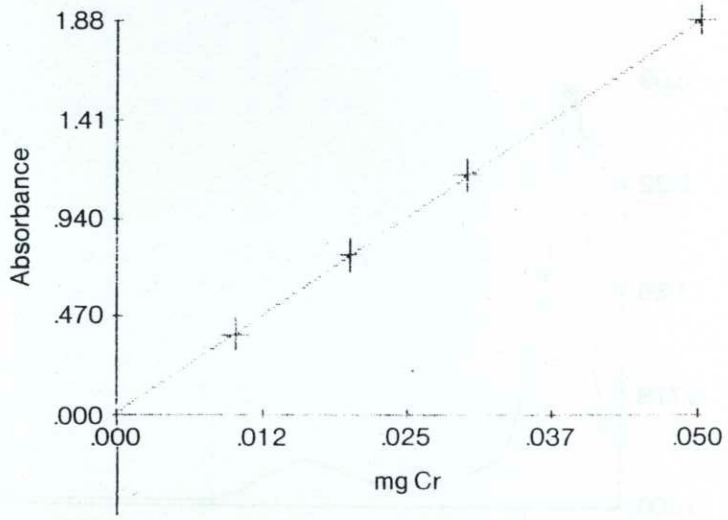

Figure 3

Calibration curve of chromium-diphenylcarbazide complex. Absorbance versus mg chromium.

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OPERATOR    JULIE             8.12.1981

DISCFILE NAME = CHROMIUM 6+

SAMPLE NAME = CHROMIUM6+

OBSERVATION WAVELENGTH = 540 NM

CUVETTE PATH LENGTH = 5 CM

ACCESSORIES = NONE

SLIT WIDTH SETTING = 2 NM

COMMENTS-----
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SAMPLE NO.       CONCENTRATION
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1                4E-03 MG
2                9E-03 MG

SAMPLE NO.       CONCENTRATION
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Figure 4

Sample results obtained from DMS 90/PLUS.