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Absorption Spectrophotometry of
Chromium Acetylacetonate*

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DETERMINATION OF CHROMIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY OF CHROMIUM ACETYLACETONATE

DETERMINATION OF CHROMIUM IN SEA WATER

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Chromium has been identified as an active and essential trace element in animals and in plants^{1,2}. Its biological significance has necessitated the development of sensitive methods of determination, and several atomic absorption methods have been described. DELAUGHTER³ reported a method of chromium determination in brine at the sub-p.p.m. level by complexation with dephenylthiocarbazone followed by extraction into methyl isobutyl ketone. The absorption sensitivity of the complex was rather low (*ca.* 0.025 absorbance for 1 p.p.m. Cr); a 200-g sample was employed and the chromium content was concentrated in 10 ml of final spray solution. Another sensitive method was later reported by FELDMAN AND PURDY⁴ by direct extraction of chromium(VI) into methyl isobutyl ketone, with a sensitivity of 0.006 p.p.m.

MCKAVENEY AND FREISER⁵ have shown that the chromium(III)-acetylacetonate complex can be formed in presence of excess of acetylacetonate at pH 6 under reflux conditions and that the complex can be quantitatively extracted into 1:1 acetylacetonate-chloroform. Based on this reaction, a sensitive atomic absorption method is described for sub-microgram amounts of chromium. The complexation of chromium by acetylacetonate at microgram level, optimum instrument parameters and enhancement of sensitivity of complexation and extraction have been studied and the application of this method to the determination of chromium in sea water is described.

EXPERIMENTAL

Reagents and equipment

Chromium standard solution. Spec-pure chromium powder was dissolved in warm concentrated hydrochloric acid and excess of acid was evaporated off on a water bath. The solution was diluted with *N* hydrochloric acid to give a stock solution containing 10 μg Cr/ml. Working standards were prepared freshly by dilution with water.

Hydrochloric acid was purified by distillation and saturated by hydrogen chloride generated from distillation of concentrated hydrochloric acid.

Acetylacetone and methyl isobutyl ketone (MIBK) were distilled.

A Techtron A.A.4 Atomic absorption spectrophotometer equipped with standard burner A-41 of 10 cm flame path, and a fuel-rich acetylene-air flame was used in the investigation. The source was a hollow-cathode chromium lamp (Atomic Absorption Lamps Pty., Australia).

Procedure

A 10-ml aliquot of solution containing a suitable amount of chromium(III) and buffered to pH 6-7 was refluxed for 30 min with 3 ml of acetylacetone in a 25-ml round-bottom flask fitted with a finger condenser and a small magnetic stirring bar. When the solution had cooled, a drop of *N* hydrochloric acid was added to acidify and the complex was extracted into 8 ml of MIBK by shaking for 1 min in a separatory funnel. The organic extract was adjusted to 10 ml in a volumetric flask. The yield of chromium acetylacetonate was determined by the atomic absorption technique (see below).

RESULTS AND DISCUSSION

Formation of chromium acetylacetonate at the microgram level

The effect of varying the amounts of acetylacetone on the yield of the chromium acetylacetonate complex was studied. From the relative absorbance obtained by the atomic-absorption measurements, it was concluded that 2-4 ml of acetylacetone was optimal for the complexation of 3 μ g of chromium(III) in 10 ml of aqueous solution. Amounts less than 2 ml or more than 4 ml resulted in low yields of the complex. It is probable that less than 2 ml of acetylacetone provides an insufficient excess of reagent, whereas more than 4 ml increases the viscosity effect, and thus lowers the feed-rate in the final spray solution because the excess of acetylacetone is extracted into MIBK.

Theoretically, an increase in the hydroxyl ion concentration should favour the formation of acetylacetonates, but no increase in yield was observed when the reaction was carried out at pH 9 by addition of pyridine. The yield was found to be optimal at pH 6-8, and was slightly low at pH 5. Reflux times of 20-60 min had no effect on the yields; a time of 30 min was chosen for convenience.

Optimum instrument parameters for atomic absorption

The optimum instrument parameters were modified slightly from those given by ALLAN⁶ for chromium in aqueous solution. The most sensitive resonance line, 3579 Å, of chromium was used. Variations in the cathode-lamp current from 8 to 10 mA and in the slit-width from 76 to 125 μ caused very little change in the sensitivity of the method. For the acetylene-air mixture used, a fuel-rich flame was found to give optimal sensitivity in the usual way. However, when the combustible organic solvent was used as spraying medium, the fuel gas had to be reduced to minimise the noise. Suitable flame mixtures were obtained by adjusting the air to 23 psi and gradually increasing the acetylene flow with pure solvent spraying in, until the luminous feather was about 2 inches long and gave the maximum absorption signal compared to the solvent blank. Under the optimal instrumental conditions, the sensitivity for chromium was 0.015 p.p.m. for 1% absorption.

The optimum instrumental conditions are summarised below:

Spectral line	3579 Å	Gas mixture	Acetylene setting at 3.5 flow meter reading
Cathode-lamp current	8–10 mA		Air 23 psi
Slit-width	100 μ	Flame path	10 cm
		Scale expansion	5×

A comparison of the absorption sensitivity under the same conditions of scale expansion and flame path, was made with chromium in aqueous solution and also with the very sensitive chromium method proposed by FELDMAN AND PURDY⁴, the chromium(VI) extract in MIBK being prepared as recommended by these authors. Other instrumental parameters such as optimal flame mixture and flame profile were determined empirically for each spraying solution. The absorption sensitivities expressed as concentration of chromium to give 1% absorption above the blank, are compared in Table I. It was found that with acetylene–air flames, the Cr(III)–acetylacetonate in MIBK was more sensitive than the Cr(VI)–MIBK, and in comparison with chromium in aqueous solution, the present complexation and extraction enhanced the sensitivity by a factor of two times.

TABLE I

ABSORPTION SENSITIVITY OF CHROMIUM (1% ABSORPTION ABOVE BLANK)

<i>Solvent</i>	<i>Chromium concn. (p.p.m.)</i>
Chromium(III)–water	0.030
Chromium(VI)–MIBK	0.024
Chromium(III)–acetylacetonate in MIBK	0.015

The high sensitivity (0.006 p.p.m. Cr for 1% absorption) given by FELDMAN AND PURDY for chromium(VI) extracted into MIBK was achieved by passing the light beam 5 times through the burner system, with a 10× scale expansion⁴.

Calibration curve

Aliquots of standard solution containing increasing amounts of chromium from 1 to 10 μg were diluted to 10 ml and complexed with acetylacetonate as previously described. The linearity of the calibration curve (Fig. 1) obtained indicates that the acetylacetonate yield is constant over the range studied. Other calibration curves for chromium in aqueous solution and for chromium(VI) in MIBK were also shown for comparison.

Interferences

The interference of diverse ions was studied by mixing 100 μg of each of the following cations with 3 μg of chromium in 10 ml of solution and carrying through the whole procedure: iron(III), molybdenum(VI), vanadium(V), titanium(IV), aluminium(III), calcium and sodium. No interference in absorption signal was observed. Iron(III) in amounts greater than 150 μg was found to interfere. Since all the above-mentioned and many other cations readily form complexes with acetylacetonate

under ordinary conditions, they can be separated quantitatively at pH 2 from the aqueous phase by extraction with 1:1 acetylacetone-chloroform⁷. When this solvent extraction is incorporated before the acetylacetonation of chromium, up to 1000 μg of each of the above cations can be readily removed by a single extraction.

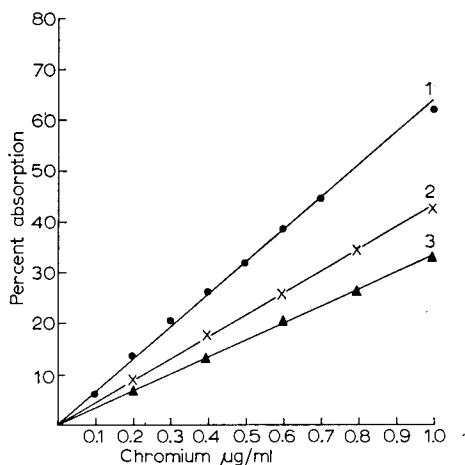


Fig. 1. Calibration curves for chromium. (1) Cr(III)-acetylacetonate in MIBK; (2) Cr(VI) in MIBK; (3) Cr(III) in aqueous solution.

DETERMINATION OF CHROMIUM IN SEA WATER

Concentration of chromium

Chromium in trace amounts can be concentrated by coprecipitation with hydrous oxides of iron(III) or aluminium, or by cocrystallization with dibromooxine⁸, or by extraction with ammonium pyrrolidine dithiocarbamate⁹. Since the water samples are generally large, direct extraction is not convenient. The final solution of dibromooxine was found to give serious interference and flame noise. Concentration by chelating resin followed by elution with acid¹⁰ and several chelating agents was also tested, but the recovery of 5 μg of chromium(III) from Chelex 100 on elution with 6 *N* hydrochloric acid was only *ca.* 55–60%, probably because of hydrolysis¹⁰. Coprecipitation with iron(III)⁸ was therefore employed.

Recommended procedure

Acidify the sample (5 l) to pH 2 immediately after collection and filter through a 0.5- μ membrane filter. Add with stirring a portion of iron(III) chloride solution containing 15 mg of iron. Adjust the pH to 8–9 with dilute ammonia and allow the precipitate to settle overnight. Siphon the supernate through an acid-washed glass-fiber filter and separate the bulk of the precipitate by centrifugation. Wash the precipitates on the filter and in the centrifuge tube with 15–20 ml of 0.5% ammonium nitrate. Dissolve the precipitate in the minimum amount of 2 *N* hydrochloric acid (5 ml), evaporate the solution almost to dryness and then dilute to *ca.* 10 ml with water. Adjust the pH of this solution to 1–2 and extract the iron with successive 10-ml portions of 1:1 acetylacetone-chloroform until the red iron complex is removed.

Adjust the pH of the aqueous phase to 6-7 with dilute ammonia and continue with the acetylacetonation of chromium as described above.

Calibrate the method by refluxing 3 μg of chromium(III) in 10 ml of solution with acetylacetone, and carry through the complete extraction procedure. Prepare the blank by refluxing a 10-ml aliquot of distilled water with 3 ml of acetylacetone and proceeding as for the sample. The final extract of the chromium acetylacetonate in MIBK is sprayed into the flame for absorption measurement as described above.

Results

The recoveries of chromium by this method were checked by introducing known amounts of chromium(III) into chromium-free sea water (2.l). The results (Table II) indicate that the recoveries are satisfactory over the range of chromium occurring naturally in sea water.

TABLE II
RECOVERIES OF CHROMIUM(III) FROM SPIKED SEA WATER

<i>Cr(III) added</i> (μg)	<i>Cr recovered</i> (μg)	<i>Cr(III) added</i> (μg)	<i>Cr recovered</i> (μg)
1	0.95	8	7.70
2	2.04	10	9.60
5	4.85		

The reproducibility of the procedure was evaluated by analyses of five 5-l surface samples taken from the South China Sea approximately 100 miles off Hong Kong. The chromium content was found to be $1.59 \pm 0.06 \mu\text{g/l}$.

SUMMARY

A sensitive atomic absorption method is described for the determination of chromium at sub-microgram levels. Chromium(III) is converted to its acetylacetone complex and extracted into MIBK. The atomic absorption sensitivity is thus enhanced two-fold compared to chromium(III) in aqueous medium. The detection limit of chromium is 0.015 p.p.m. with an acetylene-air flame; the sensitivity obtained with other chromium methods under the same instrumental conditions is compared. The method can be applied to the determination of chromium in sea water; at a level of *ca.* 1.6 $\mu\text{g Cr/l}$, the precision is $\pm 0.06 \mu\text{g/l}$.

RÉSUMÉ

On décrit une méthode sensible pour le dosage du chrome (à l'échelle sub-micro) par absorption atomique. Le chrome(III) est complexé par l'acétylacétone et extrait dans MIBK. La sensibilité de l'absorption atomique est ainsi augmentée, deux fois par rapport au chrome en solution aqueuse. La limite de détection du chrome est de 0.015 p.p.m. avec une flamme acétylène-air. On compare la sensibilité avec celles obtenues dans des conditions instrumentales similaires. Ce procédé peut être

appliqué au dosage du chrome dans l'eau de mer; pour une teneur en chrome d'environ $1.6 \mu\text{g Cr/l}$, la précision est de $\pm 0.06 \mu\text{g/l}$.

ZUSAMMENFASSUNG

Eine empfindliche Methode zur Bestimmung von Chrom im Submikrogramm-Bereich mit Hilfe der Flammenabsorptionsspektralanalyse wird beschrieben. Das Chrom(III) wird dabei in den Acetylacetonat-Komplex überführt und mit Methylisobutylketon extrahiert. Die Absorptionsempfindlichkeit wird dadurch doppelt so gross wie bei Verwendung eines wässrigen Mediums. Mit einer Acetylen-Luft-Flamme wird eine Nachweisgrenze von 0.015 p.p.m. Chrom erreicht. Die Methode kann zur Bestimmung von Chrom in Seewasser angewendet werden. Bei einem Gehalt von ca. $1.6 \mu\text{g Cr/l}$ beträgt die Reproduzierbarkeit $\pm 0.06 \mu\text{g/l}$.

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