Analysis of Chromium in Natural Waters by Gas Chromatography

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■ An analytical method for the determination of chromium in natural waters by gas chromatography techniques has been developed. The chromium is chelated with HTFA and the chelate is extracted into benzene. The extract is injected into a gas chromatograph using an electron capture detector. A detection limit of 0.1 μg/l. was found for chromium in natural water samples.

An accurate method for the determination of chromium in natural waters is essential if the true behavior of the element and its low level physiological effects are to be studied. The usual methods of aqueous chromium analysis, atomic absorption and uv-visible spectrophotometry are not generally feasible at extremely low chromium levels. Even with sophisticated modifications, the most optimistic limit of detection of total chromium is 0.5 μg/l. using X-ray fluorescence following preconcentration on a chelating resin (1). A flameless atomic absorption method can detect one μg/l. (2). Chromium levels in natural waters are sometimes in the order of 0.05 μg/l. (3). Therefore, routine analytical methods compatible with these levels should be developed.

Much work has been done on the determination of chromium present at low concentrations in other matrices by gas chromatography. Lunar samples (4), ferrous alloys (5), and biological samples (6–9) have been analyzed for chromium by this method. The procedure involves chelation of the chromium with a β-diketone, 1,1,1-trifluoro-2,4-pentanedione (also known as trifluoroacetylacetone and, hereafter, HFTA). Chromium TFA chelates have been found to be volatile enough for gas chromatographic analysis. By use of an electron capture detector, as little as 3×10^{-14} g of chromium can be detected (6). Based on a 5-μl injection, the relative detection limit would be 0.01 μg/l. of chromium, which is quite sufficient for the analysis of a natural water.

The problem of transferring chromium from a natural material into a benzene solution as a chelate can be accom-

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plished either by direct reaction in a sealed tube (4, 5) or by solvent extraction (10). Solvent extraction was the method of choice in this work since an aqueous media was to be analyzed.

The adaption of a gas chromatographic method for trace chromium determination in natural waters is dependent upon the optimization of the solvent extraction step and of instrumental parameters in the gas chromatographic step. This paper is concerned with the development of an analytical method for chromium in natural waters using gas chromatography.

Experimental Procedures

Apparatus. A Varian Aerography 1720-45 gas chromatograph equipped with a nickel 63-electron capture detector was used for all analytical work.

The radiochromium was counted on a Packard TriCarb Liquid Scintillation Spectrometer, Model 3320.

Digestions were made using a 450-W uv lamp in a water-cooled apparatus.

Reagents. Trifluoroacetylacetone (Pierce Chemical Co.) was distilled and the 105–106°C fraction was diluted to 0.164 M with high purity benzene (Fisher Scientific Co.).

A sodium acetate buffer solution of pH 5.2 was prepared by dissolving 1.25 mol of sodium acetate, either anhydrous or trihydrate, and 12.5 ml of glacial acetic acid in water and diluting to 1 l. A 0.2 M sodium sulfite solution (freshly prepared) was used to reduce $Cr(VI)$ to $Cr(III)$.

Radiochromium (^{51}Cr) as both Na_2CrO_4 and $CrCl_3$ was purchased from New England Nuclear. The scintillation cocktail was composed of 0.45 g of 1,4-bis-2(4-methyl-5-phenyloxazolyl) benzene (dimethyl POPOP), 10.5 g of 2,5-diphenyloxazole (PPO), 75 g of naphthalene and 300 ml of cellusolve (an antifreeze agent), diluted to 1 l. with 1,4-dioxane.

Standards for the gas chromatographic work were prepared from commercially available $Cr(TFA)_3$ (Pierce Chemical Co.). Weighed amounts of solid were dissolved in benzene and diluted to appropriate concentrations.

The ion-exchange resin used was Dowex 1-X8 anion-exchange resin in the chloride form.

Analytical Procedure. The preferred method of analysis used 25 ml of the water to be analyzed and was carried out in a 125-ml separatory funnel which had been washed with 1:1 HCl. One milliliter of freshly prepared sodium sulfite solution and 2.5 ml of buffer were added. A 25-ml aliquot of the 0.164M HTFA in benzene was then added and the funnel was shaken for 2 h on a mechanical shaker. The water layer was withdrawn and discarded. The benzene layer was then washed for 10 s with 25 ml of 0.1N NaOH to remove unreacted HTFA. The NaOH layer was withdrawn and discarded. The benzene solution was dried over sodium sulfate to remove remaining water. The solution was then ready for gas chromatographic analysis.

Samples subjected to the ion-exchange step used 50 ml of water. The water was mixed with the resin (1 g), and the resulting slurry was poured into a ½-in. i.d. column. The last 25 ml of water collected were used for the chromium analysis.

Digestion of the samples under the ultraviolet lamp was carried out in porcelain dishes for 4.5 h. Only 25 ml of the digested sample were analyzed for chromium.

For studies of solvent extraction efficiencies, $^{51}Cr(III)$ and $^{51}Cr(VI)$ were used as tracers. To determine the most favorable extraction conditions, many variables such as solvent volume, HTFA concentration in the benzene, shaking time, and pH were investigated. Upon completion of the extraction, both layers were sampled with a 50-μl Eppendorf pipet and placed in individual scintillation vials.

In the extraction efficiency experiments, the solvent extraction efficiency, E, was computed by multiplying the corrected counts obtained from the 50-μl aliquot by a volume factor to obtain the total number of counts in either the benzene or water layer. The number of counts in the benzene phase divided by the total number of counts in both phases was considered the efficiency.

Scintillation Counting. A 10-ml aliquot of scintillation cocktail was placed in a counting vial to which the 50-μl sample was added. If a benzene sample were added, 50 μl of water were added to that vial. Similarly, 50 μl of benzene were added to water samples. This technique approximately equalized the quenching from sample to sample. The volume of the solution to be counted was then adjusted to 15 ml with 1,4-dioxane, shaken for a few seconds, and placed in the counter.

The radiochromium was counted at 80% gain in a 50–1000 window for 10 or 20 min, depending on the activity of the sample. The sample was then counted against an external standard for 1 min in a window from 200–1000 at 1.2% gain. The corrected counts were obtained from a quench curve determined by artificially quenching known samples with nitromethane and noting the external count values.

Gas Chromatography. Best results were obtained using a ⅛-in. i.d., 6-ft long glass column packed with 0.32% OV-11 on 60/80 mesh GLC-110 glass beads. On-column injection was used to avoid injection port problems. All quantitative work utilized the following optimized parameters:

Detector	^{63}Ni electron capture
Range	10^{-10} amp/mV
Detector temperature	210°C
Injector temperature	160°C
Column temperature	140°C
Carrier gas	Prepurified nitrogen
Gas flow	40 ml/min
Attenuation	4

Injection onto the column was made with a 10-μl syringe. A small amount of air was drawn into the needle followed by the sample, which was measured entirely between calibrations within the glass barrel. When injected, the entire sample was vaporized. Between injections, the syringe was cleaned with benzene.

Quantitative determination was made by measuring the height of the trans $Cr(TFA)_3$ peak (the compound exists as cis-trans isomers in a ratio of 1:4). Picograms of chelate were plotted vs. peak height for the standard curve made from the standard solution. Unknown samples were determined in terms of picograms of chelate per injection volume.

Sampling of Natural Waters. Water samples were collected in a 4-l. lucite sampler similar to an oceanographic Van Dorn sampler. A brass messenger was used to trip the sampler at a depth midway between the surface and the bottom of the water body to be sampled. The water was then poured into a 1-l. polyethylene bottle washed with 1:1 HCl, rinsed with distilled water, and rinsed with the water to be sampled. The samples were stored at 4°C and analyzed within 48 h.

Results and Conclusions

Extraction. The addition of known amounts of ^{51}Cr to water samples followed by solvent extraction under various conditions yielded the optimum parameters used in the subsequent environmental analysis. Variation of the ratio of benzene volume to water volume under constant conditions revealed that the use of 25 ml of benzene HTFA per 25 ml of sample, a 1:1 volume ratio, gave the highest extrac-
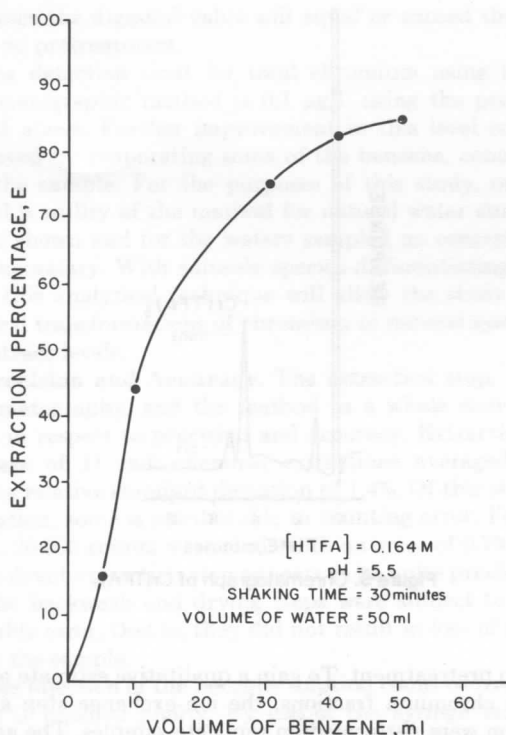
Figure 1. Variation of extraction efficiency with benzene volume

[HTFA] = 0.164 M
pH = 5.5
SHAKING TIME = 30 minutes
VOLUME OF WATER = 50 ml

Figure 2. Effect of concentration of trifluoroacetylacetone on the extraction efficiency of Cr(III)

pH = 5.5
SHAKING TIME = 2 hours
BENZENE TO WATER RATIO = 1:1

tion percentage (Figure 1; note that 50:50 ml were used). No attempt was made to account for the solubility of benzene in water. Total extraction was deemed to imply that the final concentration of chromium in terms of $\mu g/l$. in the benzene layer was equal to the original concentration of chromium in the water.

The concentration of HTFA in the benzene was found to be critical for optimized extraction. At constant pH, shaking time, and benzene volume, the larger the concentration of HTFA in the benzene, the greater the extraction percentage (Figure 2). The increase in E on going from $0.082M$ to $0.164M$ HTFA was slight, but the use of the more concentrated solution allowed more leeway for error in preparing the organic phase.

Variation of the pH of extraction revealed the optimum pH range to be from 5.0–5.5 for a $0.164M$ HTFA solution (Figure 3). In this study, use of the acetate buffer adjusted the pH of all of the water samples to this interval. Basic pH values for extraction study were difficult to maintain without going to another buffering system due to the acidity of HTFA.

The removal of samples from a separatory funnel at various times during an extraction run helped determine the optimum shaking time. Two hours of shaking at room temperature consistently gave 95% extraction or better. Any further shaking was not felt to be worthwhile. Figure 4 illustrates the observable kinetics of the extraction relating the shaking time to the ratio of found chromium (after extraction in the water phase) to the chromium originally present (C_f/C_o). The reaction appears to be first order with respect to the chromium concentration. All extractions were conducted with chromium concentrations below 10 $\mu g/l$. and HTFA in great excess ($0.164M$).

Although Cr(III) presented no difficulties during extraction, Cr(VI) extraction proved to be very erratic. Reduction of Cr(VI) to Cr(III) with Na_2SO_3 prior to extraction effectively eliminated the erratic results. The use of this particular reducing agent was dictated by its relatively inert effect upon the extraction system.
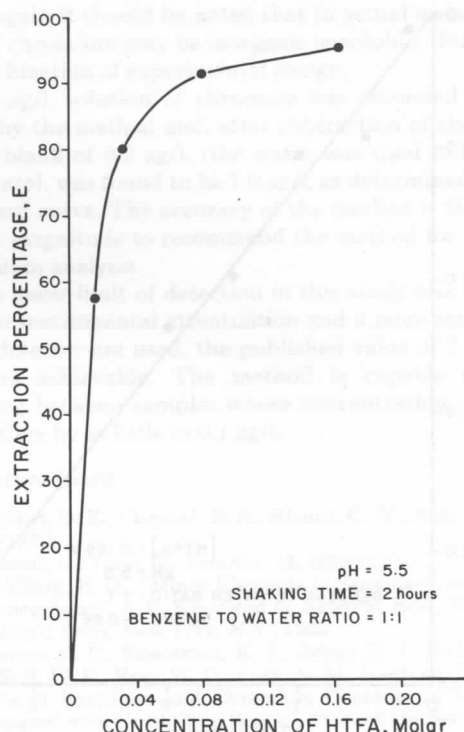
Although not all possible interferences were studied, high levels (g.t. 2 mg/l.) of Cu, Fe, Zn, Ni, Cd, Mn, Pb, and PO_4 were added to separatory funnels with 10 $\mu g/l$. of ^{51}Cr. The extraction efficiency was not in any way affected. Chromium 51 was also added to ocean water and was recovered at the 95% level. Thus, interferences do not appear to be a major problem in the use of this technique for natural water studies.

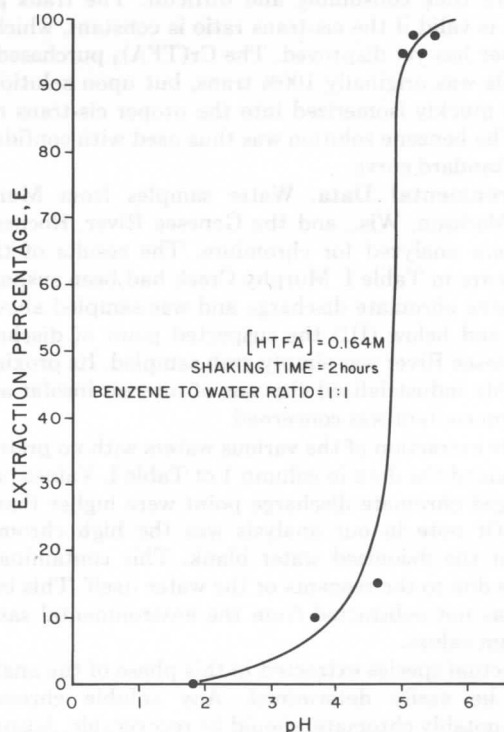**Gas Chromatography.** The gas chromatography of Cr(TFA)$_3$ has been documented previously (see refer-

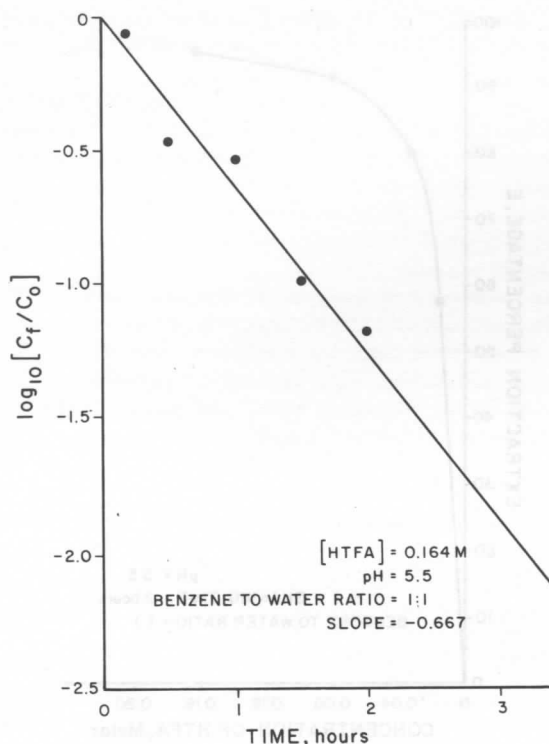Figure 3. Effect of pH on the extraction efficiency of Cr(III)

[HTFA] = 0.164M
SHAKING TIME = 2 hours
BENZENE TO WATER RATIO = 1:1

Figure 4. Rate of extraction reaction

Plot with y-axis $\log_{10}[C_f/C_0]$ and x-axis TIME, hours. Annotations:

$[\text{HTFA}] = 0.164\,M$
$pH = 5.5$
BENZENE TO WATER RATIO = 1:1
SLOPE = −0.667

Figure 5. Chromatograph of Cr(TFA)$_3$

Plot with y-axis RESPONSE and x-axis TIME, minutes. Peaks labeled Cr(TFA)$_3$, ---trans, ---cis.

ences). Many workers have not attempted to separate the isomers and none have used an OV-11 column. The column used in this investigation eluted the trans peak in 4.5 min with adequate separation of the isomers (Figure 5). This retention time appears to be the best of any yet reported in the literature. Use of an OV-11 column could shorten the GC aspect of chromium analysis and make the method more amenable for routine analysis.

The use of the trans peak for quantitative work was dictated by the convenience of measuring its height. Planimetry or total peak integration may be more accurate but are also more time consuming and difficult. The trans peak analysis is valid if the cis-trans ratio is constant, which no researcher has yet disproved. The Cr(TFA)$_3$ purchased for standards was originally 100% trans, but upon solution in benzene quickly isomerized into the proper cis-trans ratio of 1:4. The benzene solution was thus used with confidence for the standard curve.

Environmental Data. Water samples from Murphy Creek, Madison, Wis., and the Genesee River, Rochester, N.Y., were analyzed for chromium. The results of these analyses are in Table I. Murphy Creek had been suspected of receiving chromate discharge and was sampled above (I and II) and below (III) the suspected point of discharge. The Genesee River was simply grab sampled. Its proximity to a highly industrialized city was of interest insofar as its chromium content was concerned.

Simple extraction of the various waters with no pretreatment yielded the data in column 1 of Table I. Values below the alleged chromate discharge point were higher than all others. Of note in our analysis was the high chromium value for the deionized water blank. This contamination could be due to the reagents or the water itself. This blank value was not subtracted from the environmental sample chromium values.

The actual species extracted in this phase of the analysis cannot be easily determined. Any soluble chromium species, notably chromate, should be recoverable. Adsorbed Cr(III) and organic forms may or may not be extracted util-

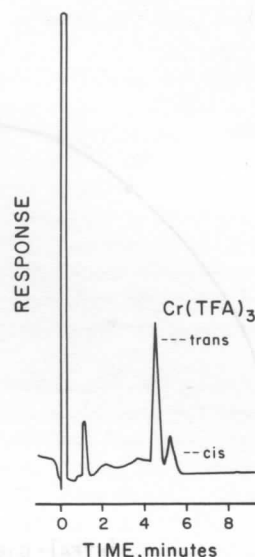izing no pretreatment. To gain a qualitative estimate of the various chromium fractions, the ion-exchange step and a digestion were performed on replicate samples. The anion-exchange resin removed any chromate, leaving only soluble trivalent species. The results show that the contaminated samples contained far less chromium after being subjected to ion exchange, while the other samples did not gain or lose significant amounts of chromium.

The digestions were carried out with ultraviolet light; thus the contamination should be minimal. Every digested sample, however, whether contaminated or not showed a significant rise in chromium. Even the deionized water showed some increase. The digested samples should be composed of total chromium in all forms, both inorganic and organic. The existence of organic chromium forms can be theorized to account for this rise but cannot be proven. The existence of transformed chromium from sources farther upstream also cannot be ignored.

In Table I, for no pretreatment, the numbers represent the total inorganic (or an operationally defined component composed of inorganic and labile organic forms). The ion-exchange step removes the chromate and gives an estimate of soluble Cr(III). The difference between the results in the first two columns is an estimate of the total chromate in solution. The digested samples should release organically bound Cr forms. This number ideally represents the total amount of chromium in all forms that are not present. In

Table I. Analysis of Environmental Samples[a]

Sample	Concentration of chromium, µg/l.		
	No pretreatment	Ion exchange	Digested
Deionized water blank	0.2 (2)	0.6 (1)	0.8 (1)
Murphy Creek I above discharge	0.4 (2)	0.4 (1)	2.4 (1)
Murphy Creek II above discharge	0.5 (2)	0.4 (1)	2.3 (1)
Murphy Creek III below discharge	1.9 (6)	0.4 (1)	2.5 (1)
Genesee River	0.3 (2)	—	—

[a] Numbers in parentheses are the number of samples run.

all cases the digested value will equal or exceed the value with no pretreatment.

The detection limit for total chromium using the gas chromatographic method is 0.1 μg/l. using the procedure noted above. Further improvement in this level could be achieved by evaporating some of the benzene, concentrating the sample. For the purposes of this study, only the possible utility of the method for natural water study was to be shown and for the waters sampled no concentration was necessary. With suitable species-differentiating methods, this analytical technique will allow the study of the natural transformations of chromium in natural systems at ultratrace levels.

Precision and Accuracy. The extraction step, the gas chromatography, and the method as a whole were evaluated in respect to precision and accuracy. Extraction percentage of 11 radiochemical extractions averaged 97.3% with a relative standard deviation of 1.4%. Of this standard deviation, some is attributable to counting error. For most vials, 20 000 counts were made with an error of 0.7%. Thus, the solvent extraction step appears to be quite precise.

The backwash and drying steps were subject to no detectable error; that is, they did not result in loss of activity from the sample.

The injection of the benzene solution could be irreproducible if handled poorly. By use of the syringe technique mentioned previously, the relative standard deviation of five replicate, 1-μl injections was 5.4%. Five injections of 2-μl had a RSD of 2.0% and six replicate, 3-μl injections had a relative standard deviation of 1.3%. The maximum injection onto a $\frac{1}{8}$-in. i.d. column is about 5 μl; so, in general, the larger the injection volume, the greater the precision.

Six replicate environmental samples (Murphy Creek III, Table I) were analyzed and proved to contain 1.9 μg/l. with a standard deviation of 2.6%. When we consider the low concentrations studied, a relative standard deviation of 10% would be good; this technique offers even better precision.

The recovery of 95% of the added inorganic soluble radiochromium in the extraction experiments attests to the accuracy of the solvent extraction step of the procedure.

Once again it should be noted that in actual water samples not all chromium may be inorganic or soluble; thus, accuracy is a function of experimental design.

A 1-μg/l. solution of chromate was extracted and analyzed by the method and, after subtraction of the distilled water blank of 0.2 μg/l. (the water was used to dilute the chromate), was found to be 1.0 μg/l. as determined from the standard curve. The accuracy of the method is thus of sufficient magnitude to recommend the method for ultratrace chromium analysis.

The lower limit of detection in this study was 10^{-12} g. If a lower instrumental attentuation and a more sensitive tritium detector are used, the published value of 3×10^{-14} g appears achievable. The method is capable of distinguishing between samples whose concentration of chromium differs by as little as 0.1 μg/l.

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