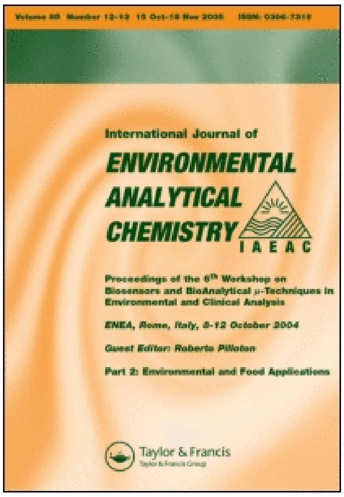

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Analytical Chemistry of Chromium Species in the Environment, and Interpretation of Results

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Analytical Chemistry of Chromium Species in the Environment, and Interpretation of Results†

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Valence-selective species determination of chromium in environmental and biological material presents intricacies primarily due to the complex nature of the samples and the instability of the oxidation states of chromium. In particular organic matter ubiquitously present in environmental samples introduces the risk of chromium(VI) reduction during analysis which takes place preferably in acidic solution. Also chromium(III) oxidation may occur in alkaline medium. Hence analytical methods should be adequately adapted to the reliable determination of chromium(VI) in blood, natural water, effluents, sediments and soil.

It can be shown that polarography is most effectually suitable to the determination of chromium(VI) compounds. Chromium(VI) is electrochemically active over the entire pH range, so that medium pH can be selected for measuring, thus protecting samples most effectively from undergoing redox reactions during the analytical procedure.

Other established methods such as spectrophotometry or valence-specific extraction are more crucial, because these generally require acidic medium.

In some cases sample pre-treatment can be employed to eliminate reductants prior to final measurement. Very few methods are available to selectively measure

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chromium(III). Indirect determination is therefore preferred. Optimum conditions for the determination of total chromium by AAS are shortly outlined.

KEY WORDS: Chromium, speciation, organic matrices, transformation, redox reactions, polarography, sample pre-treatment, extraction, sensitivity, spectrophotometry, atomic absorption spectrometry.

INTRODUCTION

Chromium belongs to the category of problematic elements in analytical chemistry because it behaves as a valence chameleon. Accordingly, most extensive efforts have been made to selectively determine the main oxidation states: tri- and hexavalent chromium. This valence-specific chromium determination is indispensable in the field of environmental and biological analysis because both oxidations states of chromium compounds cause significantly different effects:

Chromium(VI) is classified to be toxic whereas chromium(III) is substantially harmless. It belongs even to the essential components. As a consequence, most attention is paid to chromium(VI) determination in environmental and biological matter. Unfortunately, just that task is difficult to handle. Intricacies are primarily due to the instability of the oxidation states of chromium and the complex character of environmental matrices.

Chromium(VI) reduction by organic matter, normally present in those samples, must be considered as major interference.

The redox problem has not always been given adequate attention in environmental analysis. This will be shown in the following examples, which demonstrate inadequate, unreflected application of well-established analytical methods to environmental material.

A newer publication[1] about automatic measurements of chromium(VI) in waste water, capable of processing a large number of samples, reported on good engineered equipment for spectrophotometric flow measurement. The method itself was based on the diphenyl carbazide reaction in strongly acidic solution, thus introducing the risk of chromium(VI) reduction by waste water constituents. Thus the method was in fact automatic, but not adequate to the given problem.

Errors may also be produced by oxidation using an official method for measurement of chromium(VI) in factory air. The procedure is based on aspirating air through alkaline absorption solution and subsequent spectrophotometric determination of chromium(VI). Self-evidently, oxidation takes place if chromium(III) is present and valence-specific determination of chromium is illusory. Although objections were made and arbitral measurements were carried out, using filters for trapping and, thus, revealing the inherent error, the method is still in use, confirming the analyst's experience that inadequate methods have a tough life.

CHROMIUM(VI) ANALYSIS

The variety of methods for chromium(VI) determination may be classified into two fundamental categories.

1) Valence-specific, direct *measurements* such as spectrophotometry or electrochemical methods.
2) Valence-specific *separation methods*, based on selectively removing one chromium species from the sample and subsequent unspecific measurement by means of straightforward methods such as atomic absorption or emission spectrometry. The separation step comprises primarily ion-exchange and chromatography,[2–9] extraction[10–17] or co-precipitation procedures.[18–21]

A survey of established methods of the separation type is given in Table I.

It has been proved, that the indirect valence-selective determination based on separation is often not a real solution to the given problem of valence speciation. Inherently, separation procedures are not highly selective and must therefore be adjusted to the sample to be analysed and, as a prerequisite, the matrix composition must be well-defined. This requirement is often not met with environmental samples because of the complex and occasionally unspecified composition. Thus, side-reactions and erroneous results may occur. In particular extraction and ion-exchange methods, most widely used in this field, are subject to considerable errors. For example: The established ion-exchange methods are based on the assumption, that

Table I List of publications, referring to valence-speciation of chromium by means of separation techniques

Extraction methods	Ion-exchange methods	Co-precipitation methods
M. Yanagisawa *et al.*, *Mikrochim. Acta* **1973**, 475	M. S. Cresser and R. Hargitt, *Anal. Chim. Acta* **81**, 196 (1976)	E. Nakayama *et al.*, *Anal. Chim. Acta* **131**, 247 (1981)
H. Bergmann and K. Hardt, *Fresenius* **297**, 381 (1979)	A. Mazzucotelli, C. Minoia and others, *Atom. Spectr.* **4**, 182 (1983)	A. J. Pik, J. M. Eckert and K. L. Williams, *Anal. Chim. Acta* **124**, 351 (1981)
J. Pavel *et al.*, *Fresenius* **321**, 587 (1985)	A. Miyazaki and R. M. Barnes, *Anal. Chem.* **53**, 364 (1981)	R. E. Cranston and J. W. Murray, *Anal. Chim. Acta* **99**, 275 (1978)
M. H. Davis and V. B. Grossmann, *Analytical Biochemistry* **44**, 339 (1971)		T. Jan and D. R. Young, *Journal WPCF* **1978**, 2327
G. Devoto, *Bolletino d. Soc. Ital. di Sperim* **44**, 1251 (1968)		
K. Fukamachi, M. Yanagawa and others, *Japan Analyst* **21**, 26 (1972)		
W. Slavin, *Atom. Spectr.* **2**, 163 (1981)		

chromium(III) definitely forms cations so that anions, collected on a column, are considered as chromium(VI) per definitionem. This premise, however, doesn't hold for chromium(III) complexes which may be present in anionic form and thus chromium(VI) may be reflected.

Along the same lines, criticism must also be applied to the variety of selective extraction methods for chromium(VI), being especially popular because of the ease of operation and rapid performance. All these methods are based on reaction of chromium(VI) with organic agents such as dithiocarbamates, extraction of the complexes formed and subsequent unspecific chromium determinations by, for example, atomic absorption spectrometry. The crucial point of this principle is the risk of co-extraction of chromium(III) complexes, initially present in the sample.

From these arguments, it is evident that selective separation methods are often not suitable for valence-specific chromium determination in complex material. Despite the quoted limitations, however, numerous procedures of this type are used in environmental analysis. In these cases it is indispensable to critically consider the individual task and to check as to whether the matrix is such that separation methods may be utilized.

The most promising procedures for valence-specific chromium determination in the given field will be outlined in the following.

Polarography

By far the best potential provides polarographic determination of chromium(VI). Hexavalent chromium is electrochemically active over the entire pH-range, so that medium pH can be chosen throughout which offers ideal conditions for stabilizing the oxidation states of chromium. Moreover, a variety of supporting electrolytes is suitable so that the operating conditions can readily be adapted to the composition of the given sample.[22–26]

Applications with waste water raise problems because its composition is essentially unspecified.[27] In order to eliminate interferents as far as possible, polyvalent inorganic cations are removed by precipitation with phosphate buffer solution. Removal is completed by addition of aluminium sulphate as flocculant. During this treatment, co-precipitation of chromium(VI) proved to be negligible. In the residual phosphate buffer solution, chromium(VI) can readily be measured. The polarographic characteristics under these conditions are shown in the Figure 1. The curves are recorded in the differential pulse mode and it can be seen, that two peaks appear, the height of which depends on the pH. Both peaks reflect the reduction of

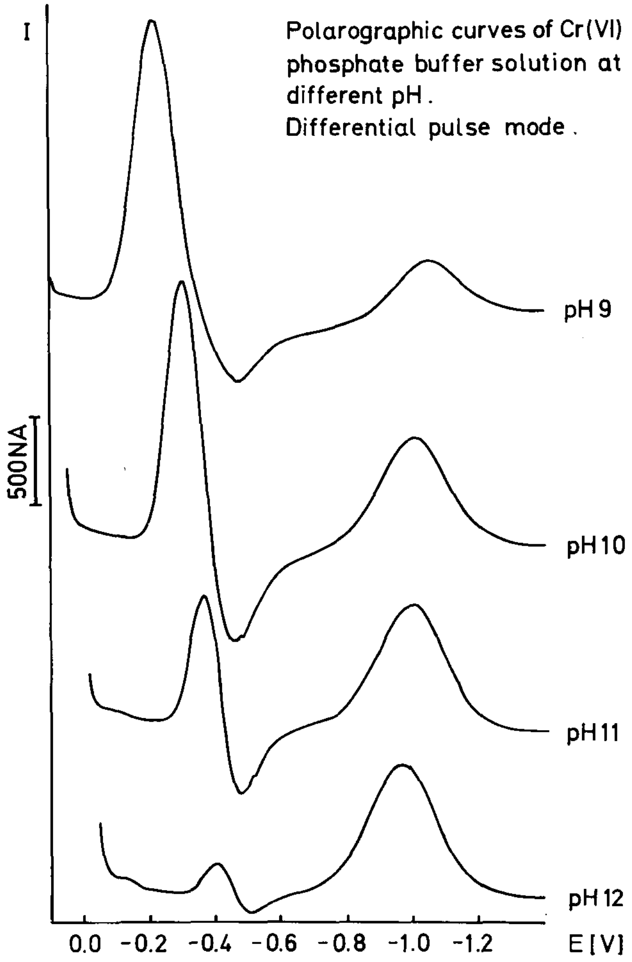

Figure 1 Polarographic curves of chromium(VI) in phosphate buffer solutions at different pH.

chromium(VI) to chromium(III), which represents an anomaly, due to surface effects on the mercury drop caused by formation of sparingly soluble chromium compounds. Quantitative considerations on this effect are published elsewhere.[27] This anomaly of having two peaks available offers practical advantages in that operating conditions are flexible and interference by electroactive organic constituents can be detected and eliminated.

The lower limit of the method is between 30 and 50 parts per billion, depending on the sample background. Figure 2 shows a typical recording for 50 parts per billion in an artificial waste water prepared for test purposes. The method has been successfully used in routine analysis for five years.

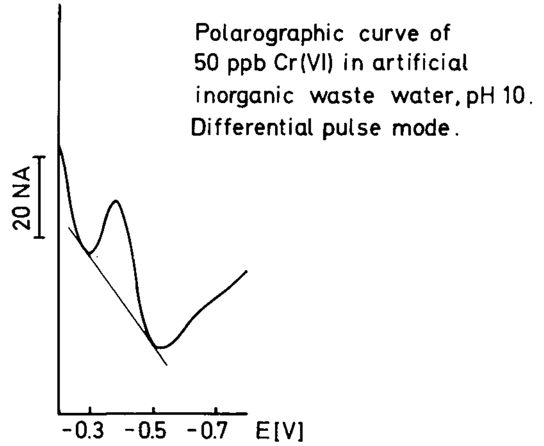

Figure 2 Polarographic curve of 50 ppb chromium(VI) in artificial inorganic waste water, pH 10. Differential pulse mode.

The method is used also for measurements on the long-term behaviour of chromium(VI) in natural and river water, sediments and slurry. Some typical results are demonstrated in the following tables.

Table II shows the behaviour of different types of river water, each spiked with 100 parts per billion chromium(VI) and stirred during the observations period. It can be seen that the chromium(VI) concentration gradually decreases with time, obviously causes by

Table II Reduction of chromium(VI) in natural water. Initial chromium(VI) concentration 100 ppb

Observation time (d)	Residual chromium(VI) and concentration (ppb)		
	River Rhine pH 8.0	Büttel Channel pH 8.1	Lake "Kremperheide" pH 7.6
3	100	100	95
7	98	95	93
14	95	88	86
56	86	78	73
112	82	70	69

organic constituents, generally occurring in natural water. The resulting chromium(III) could be detected in the sediments. The reduction rate depends considerably on the individual samples as to be expected.

Similar tests were conducted with a variety of river sediments, containing about 80% water.

From Table III it can be seen that the reduction rate in sediments is some orders of magnitude higher than in the water samples. By far the fastest reduction of chromium(VI) could be observed with fresh municipal slurries of different provenance. In these cases, small chromium(VI) amounts were reduced almost instantaneously. Moreover, the reduction capacity of this type of sample proved to be considerable. It exceeded 20 parts per million in any case.

Table III Reduction of chromium(VI) in sediments. Initial chromium concentration 2 ppm

Observation time (h)	Residual chromium(VI) concentration (ppm)		
	River Elbe	Büttel Channel	Lake "Kremperheide"
0.2	0.77	<0.02	1.86
1	0.26	—	0.06
2	0.11	—	<0.02
4	0.09	—	—
24	<0.02	<0.02	<0.02

For all these studies, polarography proved as a reliable and efficient tool, capable of handling large series of samples at flexible operating conditions.

Polarography was also used for the determination of chromium(VI) in blood and human serum. Because of the complex composition of these matrices and of the high amounts of organics, no other method could successfully be applied.

For polarographic measurements, no reagents need be added: The original sodium chloride content serves as supporting electrolyte, the original pH of about 8 is well suitable and finally, no other electroactive compounds exist in the potential range of interest. Thus, direct measurements could be made and the lifetime of chromium(VI) in blood could be studied quantitatively.

The results of model tests are given in Figure 3. It represents the concentration vs. time curve of chromium(VI) in serum which indicates comparatively rapid fading of the initial chromium(VI) concentration by 1 ppm. After that, reduction continues to occur asymptotically and the final value of chromium reduction capacity by plasma constituents is about 2 ppm. As a rule of thumb, this represents the typical reduction capacity of human plasma. There

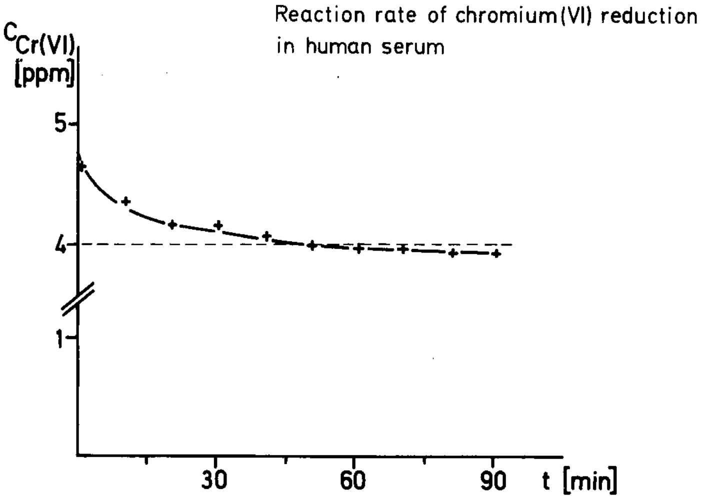

Figure 3 Reaction rate of chromium(VI) reduction in human serum.

are, however, individual differences, which can be seen in Table IV. This means, individuals may be classified as strong and weak reducers with respect to chromium(VI). On the other side, the quantitative detection of the inherent reduction capacity of human serum indicates, that small amounts of chromium(VI) are not persistent in blood, probably in other body fluids not either (see also U. Korallus, J. of Toxicological and Environmental Chemistry in press).

Table IV Reducing capacity of individual samples of human serum and plasma

Sample	Reducing capacity (ppm)
Serum 1	1.5
Serum 2	1.9
Serum 3	1.1
Serum 4	1.5
Plasma 5	1.2
Plasma 6	1.8

The effect of ascorbic acid as antidote in case of accidental poisoning with chromium(VI) compounds was also studied.[28] Figure 4 shows the reduction rate of chromium(VI) in plasma at different concentrations of ascorbic acid. Also, dose dependence can be understood from the curves.

Spectrophotometry

Despite the promising features of polarography in the given field, it does not cover all the requirements in environmental chromium analysis because of the limited sensitivity. As mentioned before, the lower limit is 30 parts per billion and may be higher depending on the type of sample. Accordingly, there is the need of testing and establishing alternative methods if very low concentrations are to be measured.

This is the case in water analysis, where the lowest concentration range for chromium(VI) measurements can not be covered by

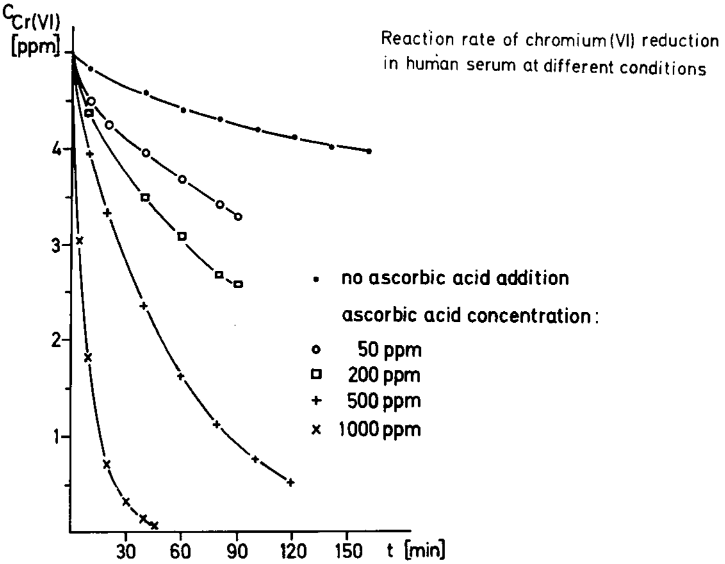

Figure 4 Reaction rate of chromium(VI) reduction in human serum at different conditions in the presence of ascorbic acid.

electrochemical measurements. Thus, it was mandatory to establish special methods for water control.

In Germany, work has been done on this subject under the auspices of the Standardization Institute DIN. During development of an adequate method for valence-specific determination of chromium(VI) covering all types of water and waste water, almost all the initially mentioned procedures were tested, including extraction, ion-exchange and co-precipitation methods. They proved essentially practicable and satisfactory in model tests and for particular types of sample, however, they failed for a large number of "real-world" samples. The well-established diphenyl carbazide reaction with chromium(VI) is in fact valence-specific, however, it is highly subject to interference by metal ions and by chromium(VI) reduction in acidic solution. Thus, extensive sample pre-treatment was required comprising the following steps: Precipitation of polyvalent cations including chromium(III) by phosphate buffer/aluminium sulphate as also applied in polarography, oxidation of strong reductants by hypochlorite addition—all these steps at medium pH—destruction of hypochlorite and finally colour development with diphenyl carbazide. Additional precaution must be taken to avoid interfering side-reactions. The method is sensitive and works well, however, it is rather sophisticated. Nevertheless, the procedure will be issued as a German Standard in the near future. It is the most universal one from a variety of other methods with inherent limitations, which may reflect the intricacies encountered in valence-specific chromium determination.

CHROMIUM(III) ANALYSIS

Selective chromium(III) determination is even more difficult than chromium(VI) determination because there are only very few specific chromium(III) reactions suitable as a basis for analytical measurement.[11,29,30]

Consequently, chromium(III) is normally obtained as a difference after determination of total chromium and chromium(VI). Total chromium determination can readily be done by plasma excited emission or atomic absorption spectrometry. The sensitivity of the latter method is better than 1 part per billion. Standardized methods for chromium determination in water and waste water are available.[31]

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