Estimation of Cr(III) in Water with the Presence of Cr(VI) by Chlorophosphonazo I Color Reaction Spectrophotometry

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A method capable of accurately and selectively measuring Cr^{3+} in water is required and was therefore studied. The precision and reproducibility of chlorophosphonazo I color reaction spectrophotometry (CCRS) for the selective determination of Cr^{3+} was improved to be acceptable standards. The CCRS established is therefore an accurate, reproducible and inexpensive method. It also has reasonably good sensitivity and selectivity, and a high sample output. This method should be readily adapted for the routine and selective determination of Cr^{3+} in bottled mineral drinking water with (or without) the supplementation of Cr^{3+} or in natural water such as mineral or pipe water with the presence of Cr^{6+}.

Keywords Selectively estimating Cr^{3+}, spectrophotometric method, accuracy evaluation, rapid, applicability

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Introduction

Chromium (Cr^{3+}) participates in the metabolism of glucose[1,2] and it is considered an essential nutrient. The deficiency of Cr^{3+} in the body could induce diabetes and other disorders.[3,4] The supplement of Cr^{3+} alleviates these disorders.[5] On the other hand, the over-intake of Cr^{3+} is highly toxic.[6]

Natural drinking water is not pure,[7] and may contain chromium. Although chromium concentration in natural water is usually low, it could be above 0.5 mg/L in some areas of the world.[8] Therefore, its presence in drink water should always be monitored. The oxidation states of Cr in water are primarily Cr^{3+} and/or Cr^{6+}. Furthermore, perhaps the lack of an accurate method for measuring the concentration of Cr^{3+} may be the reason why a limitation of 0.05 or 0.10 mg/L of total chromium in drinking water is implemented by WHO[9] and the US Environmental Protection Agency,[10] respectively. The limitations should be basically established on the toxicity of Cr^{6+}. This means that it is important and necessary for us to distinguish Cr^{3+} from Cr^{6+} in water.

An extensive literature search indicates that reported methods for measuring Cr include the following: UV-VIS spectrophotometry,[11,12] high-performance liquid chromatography,[13] high performance liquid chromatography–ultraviolet spectrophotometry,[14] atomic absorption spectrometry (AAS),[15-17] flow injection–solid phase spectrophotometry[18] and atomic emission spectrometry,[19-22] capillary electrophoresis,[23] catalytic cathodic stripping voltammetry,[24] and mass spectrometry.[25] However, the rapidly selective quantification of Cr^{3+} and Cr^{6+} still appears to be a hot point of study since they normally coexist in water.

Recently, spectrophotometry still appears to be the method that has been studied extensively for measuring Cr^{3+} and Cr^{6+}.[26-29] The discovery of a new color reaction reagent for the selective determination of Cr^{3+} or Cr^{6+} is vital for the successful application of spectrophotometry in practice. We report here a spectrophotometry (CCRS) based on chlorophosphonazo I (Fig. 1) color reaction, which is suitable for the selective quantification of Cr^{3+} with the presence of Cr^{6+}.

Experimental

Reagents and chemicals

All reagents were of analytic grade. Freshly distilled and deionized water was used. Testing solution (10 μg Cr^{3+}/mL) was prepared by dissolving chromium chloride in water. Chlorophosphonazo I solution was prepared by dissolving 0.0418 g in 250 mL water. Serial acetate buffer solutions with pH ranging from 3.5 to 5.6 were prepared by dissolving appropriate amounts of sodium acetate trihydrate and glacial acetic acid in 500 mL water. Ammonium chloride solution was prepared by dissolving 12.5 g in 250 mL water. Nitric acid (2+1) was prepared by mixing 2 parts concentrated nitric acid (*ca.* 16 N) with 1 part water.

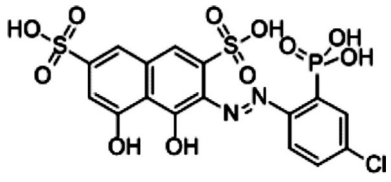

Fig. 1 Structural diagram of chlorophosphonazo I.

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General procedure of CCRS

An appropriate amount of the testing solution containing an appropriate amount of Cr^{3+} was pipetted into a 25-mL volumetric flask. Then 5.0 mL buffer solution and an appropriate amount of chlorophosphonazo I solution were added to each volumetric flask. After shaking well, the volumetric flask was heated for an appropriate time in a water bath with an appropriate temperature. After cooling to room temperature, 2.50 mL nitric acid (2+1) was added and the volume was made up to 25 mL with water. The absorbance of the colored solution was measured at 600 nm against a reagent blank prepared under similar conditions without the presence of Cr^{3+} in 2.00 cm glass cells. Ten replicates were carried out for each testing sample. The operational parameters finally established are described in *Optimization of experimental conditions* in Results and Discussion.

Spectral characteristics of Cr^{3+}-chlorophosphonazo I complex solution

The basic procedure was similar to that described in *General procedure of CCRS*. In addition, an appropriate amount of the testing solution was added to the 25 mL volumetric flask, which gave the final concentration of 2.0 μg Cr^{3+}/mL. The pH was controlled to be 3.7 by adding 5.0 mL buffer solution while the amount of chlorophosphonazo I solution added was 3.0 mL. The mixed solution in the volumetric flask was heated for 15 min in a boiling water bath. After cooling to room temperature, 2.50 mL nitric acid (2+1) was added and the volume was made up to 25 mL with water. The absorbance of the colored solution was scanned at wavelengths ranging from 480 to 640 nm against a reagent blank prepared under similar conditions without the presence of Cr^{3+}. For comparison, chlorophosphonazo I solution prepared with all reagents added except for Cr^{3+} solution was treated and also scanned at the same condition.

Optimization of experimental conditions

On the basis of the procedure described in *General procedure of CCRS*, the effect of pH (3.5 – 5.6), amount of chlorophosphonazo I solution added (1.0 – 5.0 mL), heating time (5 – 20 min) and heating temperature (70°C – boiling point) were investigated. When a parameter was investigated, all other parameters were fixed to be the same as that described in *Spectral characteristics of Cr^{3+}-chlorophosphonazo I complex solution*.

Linear relationship between measurements by CCRS and concentration of Cr^{3+}

Each of the testing solutions containing 10 (testing sample 1), 20 (testing sample 2), 30 (testing sample 3), 40 (testing sample 4) or 50 μg (testing sample 5) Cr^{3+} was pipetted into a 25-mL volumetric flask, respectively. The rest was the same as that described in *General procedure of CCRS* and the operational parameters were the same as that established in *Optimization of experimental conditions*. The final concentration of Cr^{3+} was 0.40 μg/mL in testing sample 1, 1.00 μg/mL in testing sample 2, 1.50 μg/mL in testing sample 3, 2.00 μg/mL in testing sample 4 and 2.50μg/mL in testing sample 5, respectively.

Evaluation of CCRS by using AAS as a reference procedure

AAS procedures for the determination of Cr^{3+}. Testing solutions containing 10 (testing sample 1), 20 (testing sample 2), 30 (testing sample 3), 40 (testing sample 4) and 50 μg (testing sample 5) Cr^{3+} were pipetted into a 25-mL volumetric flask containing 2.00 mL ammonium chloride solution, respectively. Then, each volumetric flask was made up to 25 mL with water. The final concentration of Cr^{3+} was 0.40 μg/mL in testing sample 1, 1.00 μg/mL in testing sample 2, 1.50 μg/mL in testing sample 3, 2.00 μg/mL in testing sample 4 and 2.50 μg/mL in testing sample 5. The determination of chromium by AAS was performed at the wavelength 357.9 nm, the spectral band-width 0.2 nm, the burner height 9 nm and the flow rate of acetylene gas 2.8 L/min. The chromium hollow cathode lamp was operated at 10 mA. Ten replicates were carried out for each testing sample.

Comparison of reproducibility test of CCRS or AAS for measuring Cr^{3+}. The data for calculating the measurement repeatability of CCRS or AAS were obtained under the repetitive condition that the measurement of the same sample (10 replicates) was carried out by using the same facilities in a short interval and in the same manner by the same operator (intra-day). The measurement repeatability limit of CCRS or AAS was calculated by using the following formula: $r = 2.8 \times \mathrm{Sr}$ (estimated value of the standard deviation).

The data for estimating the reproducibility of inter-day measurements by CCRS or AAS were obtained in two different laboratories by different operators, respectively. The average value of each sample (three replicates) measured in two different laboratories (named parallel 1 and 2) was compared with each other. The basic procedures are similar to those described in "*Optimization of experimental conditions*" in Results and Discussion and "*AAS procedures for the determination of Cr^{3+}*" above, respectively. The absolute difference of the two measurements less than or equal to the repeatability limit was considered as the condition of reproducibility at the 95% confidence level.

Correlation analysis. All the analytic results (50 measurements of 5 testing samples) were employed in conducting correlation analysis. The correlation coefficient values are in the range of –1 to +1. A positive correlation indicates that the measurements of two methods tend to be identical whereas a negative correlation shows that they tend to be different.

The difference and relative difference between the average values measured by CCRS and AAS. They were calculated by using the average values of the 5 measured results of each testing sample.

Standard deviation and relative standard deviation of all the values measured by CCRS and AAS. They were calculated by using all the values (20 measurements) of both testing samples. This was employed as the method for testing the identity of the measured values by CCRS and AAS.

Determination of Cr^{3+} in natural mineral or pipe water

The natural mineral or pipe water was concentrated 10 times *in vacuo*. The concentrated mineral (or pipe) water (1 mL) or the concentrated mineral (or pipe) water (1 mL) containing 10 μg added standard Cr^{3+} was pipetted into a 25-mL volumetric flask, respectively. The following procedures were similar to that described in *Optimization of experimental conditions* in Results and Discussion. The recovery rate of standard Cr^{3+} was obtained by calculation [*i.e.* ($MSSCr^{3+}$-$MSCr^{3+}$)/$ASCr^{3+}$] where $MSSCr^{3+}$ = the measured Cr^{3+} in natural mineral or pipe water samples with added standard Cr^{3+}, $MSCr^{3+}$ (= the measured Cr^{3+}) in natural mineral or pipe water samples without added standard Cr^{3+}, and $ASCr^{3+}$ (= amount of added standard Cr^{3+}).

Estimation of the minimum level of Cr^{3+} detectable by CCRS

Natural mineral water with a known Cr^{3+} concentration is diluted properly so as to obtain a series of samples with a concentration gradient ranging from 0.03 – 0.40 μg/mL.

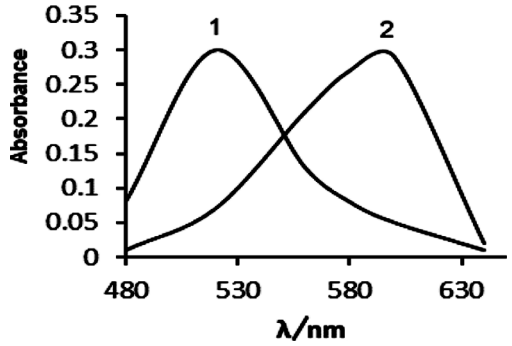

Fig. 2 VIS absorption spectra of chlorophosphonazo I solution (1) and chlorophosphonazo I-Cr^{3+} complex solution (2).

Pure water is used to give the sample containing 0.00 μg/mL Cr^{3+}. The Cr^{3+} concentration in the series of samples was determined by the method similar to that described in *Optimization of experimental conditions* in Results and Discussion.

Effect of other irons on the analytical reaction

A solution containing Fe^{3+}, Fe^{2+},Cu^{2+}, Zn^{2+}, Al^{3+}, Zn^{2+}, Ti^{3+}, Ca^{2+}, Mg^{2+}, Co^{3+} and Cr^{6+} was added to standard Cr^{3+} solution. Then, the procedure described in "*Optimization of experimental conditions*" in Results and Discussion was followed to test the interference of these ions in the analytical reaction.

Apparatus

The spectrophotometer was made by Shanghai Jinghua Technology Instrument Co., Ltd., PRC. The TAS-986 atomic absorption spectrometer used was manufactured by Beijing Purkinje General Instrument Co., Ltd., PRC. The FA1004 electronic analytical balance was made by Shanghai Hengping Scientific Co., Ltd., PRC.

Statistic analysis

The experimental data were statistically analyzed using one way ANOVA test and Microsoft Office Excel.

Results and Discussion

Spectral characteristics of Cr^{3+}-chlorophosphonazo I complex solution

The VIS absorption spectra of chlorophosphonazo I solution and chlorophosphonazo I-Cr^{3+} complex solution are shown in Fig. 2. The wavelength of the maximum absorption of chlorophosphonazo I solution without the addition of Cr^{3+} was found at 520 nm. When chlorophosphonazo I-Cr^{3+} complex was formed, the wavelength of the maximum absorption of the colored solution was found at 600 nm. Therefore, for the determination of Cr^{3+} by chlorophosphonazo I, all the measurements were recommended to be made at 600 nm. This has never been reported in the literature before.

Although an extensive literature search indicated that chlorophosphonazo I was employed for spectrophotometrically determining some metals including uranium, protactinium, cadmium, zirconium, thorium, lanthanum, yttrium, calcium, magnesium, titanium and aluminium,[30] no one has reported that measurements were made at 600 nm. Second, the operational conditions for color reaction were very different from that established in this study. Third, the mechanism of methods of determining most metals were based on the decoloration of chlorophosphonazo I. Although it seems that the determination of aluminium is based on the color of the chlorophosphonazo I-Al complex formed and the measurement is made at 610 nm, close to the wavelength used in this study, the chlorophosphonazo I-Al complex is formed at pH 4 – 6 and it can be dissociated by the addition of nitric acid (2+1).

Optimization of experimental conditions

Effect of pH. The formation of chlorophosphonazo I-Cr^{3+} complex was investigated over the pH ranging from 3.5 to 5.6. The absorbance at 600 nm was found to be maximum and constant at the pH ranging from 3.6 to 3.8. Hence, pH 3.7 (maintained by acetate buffer which was prepared by dissolving 9.0 g sodium acetate trihydrate and 4.9 mL glacial acetic acid in 500 mL water) was selected for the determination in this study.

Effect of amount of chlorophosphonazo I solution added. The color reaction between chlorophosphonazo I and Cr^{3+} was studied over the amount of added chlorophosphonazo I ranging from 1.0 to 5.0 mL. It was found that the maximum and most stable absorbance was obtained when 3.0 mL chlorophosphonazo I was added. Therefore, the addition of 3.0 mL chlorophosphonazo I was selected for the determination in this study.

Effect of heating time. Over the range of 5 – 20 min heating times studied, it was found that 14 – 20 min gave the maximum and constant absorbance at 600 nm. Since a longer time increases energy consumption and the difficulty of operation, 15 min was selected for the determination in this study.

Effect of heating temperature. Over the range of heating temperature from 70°C to boiling point investigated, it was found that only heating at boiling point was able to give the maximum and constant absorbance at 600 nm. Hence, heating at boiling point was selected for the determination in this study.

Procedure of CCRS established. An appropriate amount of sample solution containing Cr^{3+} was pipetted into a 25-mL volumetric flask, respectively. Then 5.0 mL buffer solution and 3.0 mL chlorophosphonazo I solution were added to each volumetric flask. After shaking well, the volumetric flasks were heated for 15 min in a boiling water bath. After cooling to room temperature, 2.50 mL nitric acid (2+1) was added and the volume was made up to 25 mL with water. The absorbance of the colored solution was measured at 600 nm against a reagent blank prepared under similar conditions without the presence of Cr^{3+} in 2.00 cm glass cells. Ten replicates were carried out for each testing sample.

Linear relationship between measurements by CCRS and concentration of Cr^{3+}

The relationship between the absorbance and the concentration (0.4 – 2.0 μg/mL) tested of the standard Cr^{3+} solution obeyed Beer's law (also see Fig. 3). The regression equation for the data being:

$$y = 0.0618x + 0.0054$$

The correlation coefficient was 0.9964, including the origin of coordinates (0.0, 0.0). This means that the Cr^{3+} approaching 0.0 in water could be estimated by the regression equation mentioned above, depending on the sensitivity of the spectrophotometer used. Therefore, Cr^{3+} concentration <0.4 μg/mL can also be estimated with a reasonable accuracy.

Evaluation of CCRS by using AAS as a reference procedure

Comparison of reproducibility of the values measured by CCRS and AAS. The results of the test on the reproducibility of the

values measured by different operators using CCRS or AAS in different laboratories are shown in Table 1. It can be seen that the differences of the average inter-day values measured by different operators using CCRS or AAS in two different laboratories were all less than the repeatability limit related, respectively. This test indicates that the reproducibility of the values measured by either method is good or acceptable.

Correlation analysis of the values measured by CCRS and AAS. It has been known that AAS can accurately determine Cr^{3+} without the presence of Cr^{6+}.[31] However, the determination of Cr^{3+} by CCRS based on chlorophosphonazo I has never been studied before and its accuracy remains unknown. Therefore, we used a standard solution of Cr^{3+} that does not contain Cr^{6+} to estimate the accuracy of CCRS based on chlorophosphonazo I by using atomic absorption spectroscopy as a reference method.

Figure 4 shows the scatter diagram obtained by plotting the values measured by CCRS against that by AAS (r = 0.9996, including the origin of coordinates (0.0, 0.0)); the regression equation for these data being:

$$y\ (Cr^{3+}\text{ concentration measured by CCRS, μg/mL}) = 0.9986x\ (Cr^{3+}\text{ concentration measured by AAS, μg/mL}) + 0.002$$

These mean that the values measured by CCRS correlated very well with that measured by AAS. This preliminarily implies that the precision of CCRS is identical with that of AAS for the determination of Cr^{3+}.

The difference and the relative difference between the values of each testing sample measured by CCRS and AAS. The difference and the relative difference between the average values of 5 different samples measured by CCRS and AAS are shown in Table 2. It is obvious that the relative differences between the average values of testing sample 1, 3, 4 or 5 measured by CCRS and AAS are less than 5% while only that of testing sample 2 is larger than 5%, but far less than the 10% that is considered acceptable for analyzing the component with its content less than 0.1%. These results therefore indicate that the values measured by CCRS and AAS are identical.

The standard deviation and relative standard deviation of all the values of each testing sample measured by CCRS and AAS. The analysis results of the SD and RSD of all the values measured by CCRS and AAS are shown in Table 3. This table indicates that the RSD of all the values of testing samples 1, 2, 3, 4 and 5 measured by the two methods are less than 5%, respectively. This again indicates that the values measured by CCRS and AAS are identical.

The recovery rate of standard Cr^{3+} from natural mineral or pipe water by CCRS

The amount of Cr^{3+} estimated from the curve shown in Fig. 3 by using the difference between the measurements of the concentrated mineral (or pipe) water (1 mL) or the concentrated mineral (or pipe) water (1 mL) containing 10 μg added standard Cr^{3+} was employed in calculating percent recovery. The percent

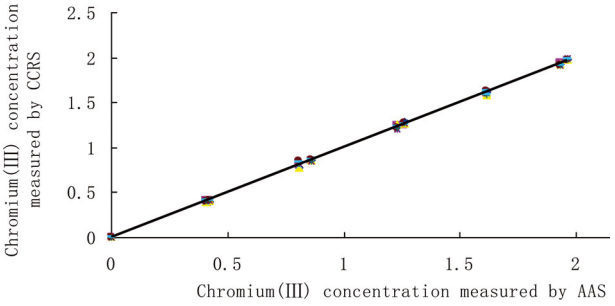

Fig. 4 The correlation between the Cr^{3+} concentrations (μg/mL) measured by CCRS and AAS.

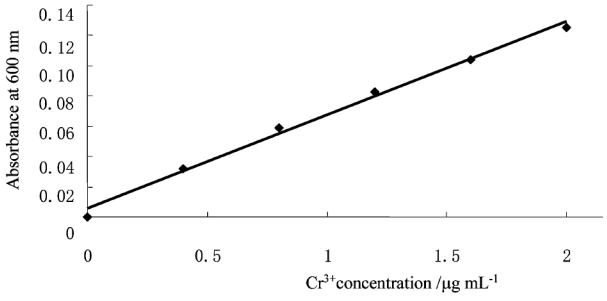

Fig. 3 The standard curve of chromium standard solution measured by CCRS.

Table 2 Difference and relative difference between the average values measured by CCRS and AAS

Testing sample	Average measured values by CCRS/ μg mL^{-1}	Average measured values by AAS/ μg mL^{-1}	Average values by CCRS and AAS/ μg mL^{-1}	Difference	Relative difference, %
1	0.4071	0.4101	0.4086	0.0030	0.73
2	0.8564	0.8124	0.8344	0.044	5.27
3	1.2694	1.2264	1.2479	0.043	3.45
4	1.6152	1.6008	1.6080	0.0144	0.90
5	1.9227	1.9779	1.9503	0.0552	2.83

Table 1 Comparison between the reproducibility of the values (μg/mL) measured by CCRS and AAS

Testing sample	CCRS				AAS			
	Parallel l	Parallel 2	Difference	Repeatability limit	Parallel 1	Parallel 2	Difference	Repeatability limit
1	0.4085	0.4057	0.0028	0.0224	0.4118	0.4083	0.0035	0.0269
2	0.8585	0.8543	0.0042	0.0252	0.8145	0.8103	0.0042	0.0560
3	1.2730	1.2658	0.0072	0.0280	1.2291	1.2238	0.0053	0.0476
4	1.6166	1.6138	0.0028	0.0196	1.6030	1.5987	0.0043	0.0364
5	1.9250	1.9204	0.0046	0.0224	1.9803	1.9754	0.0049	0.0241

Table 3 The analysis results of standard deviation and relative standard deviation of all the values (μg/mL) measured by CCRS and AAS

RP[a]	Testing sample 1		Testing sample 2		Testing sample 3		Testing sample 4		Testing sample 5	
	CCRS	AAS	CCRS	AAS	CCRS	AAS	CCRS	AAS	CCRS	AAS
1	0.4046	0.4231	0.8599	0.8077	1.2627	1.2308	1.6130	1.6154	1.9282	1.9615
2	0.4097	0.3916	0.8611	0.7799	1.2778	1.2330	1.6076	1.6214	1.9201	1.9773
3	0.4114	0.4058	0.8417	0.8116	1.2375	1.2464	1.6162	1.5942	1.9432	1.9710
4	0.3907	0.4161	0.8581	0.7810	1.2755	1.2555	1.6093	1.5839	1.9265	1.9854
5	0.3993	0.4100	0.8731	0.8100	1.2792	1.2100	1.6007	1.6100	1.9222	1.9767
6	0.4143	0.4032	0.8514	0.8159	1.2710	1.1968	1.6206	1.6085	1.9178	1.9905
7	0.4024	0.4044	0.8554	0.8433	1.2735	1.2194	1.6220	1.5956	1.9181	1.9718
8	0.4128	0.4233	0.8446	0.8221	1.2763	1.2209	1.6218	1.5890	1.9154	1.9877
9	0.4152	0.4107	0.8569	0.8182	1.2809	1.2257	1.6166	1.6019	1.9170	1.9781
10	0.4107	0.4126	0.8614	0.8343	1.2600	1.2259	1.6139	1.5873	1.9185	1.9789
AV[b]	0.4086		0.8344		1.2479		1.6074		1.9503	
SD	0.0086		0.027		0.026		0.012		0.029	
RSD	2.1%		3.2%		2.1%		0.75%		1.5%	

a. RP refers to replicates. b. AV refers to average.

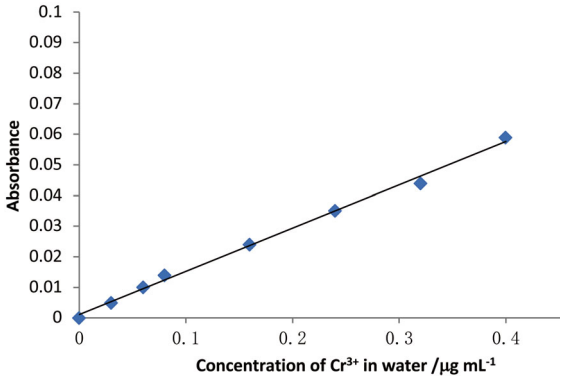

Fig. 5 Test for the minimum level of Cr^{3+} detectable by CCRS: the correlation between the absorbance measured by CCRS and Cr^{3+} concentrations ranging from 0.00 – 0.40 μg/mL.

recovery of the added standard Cr^{3+} from natural mineral or pipe water by CCRS was 99.8 or 99.7, respectively. This means that the anti-interference ability of CCRS is very good. Considering the interference of Cr^{6+} and unsuitability for directly and selectively measuring Cr^{3+} in natural mineral or pipe water, AAS was not therefore tested.

The minimum level of Cr^{3+} detectable by CCRS

The minimum concentration of Cr^{3+} tested was 0.03 μg/mL while the maximum concentration tested was 0.40 μg/mL. Regression analysis including the data obtained from the tested concentration of 0.03 – 0.40 μg/mL gave a line passing through the origin of coordinates. This means that the relationship between the absorbance and the concentration (0.00 – 0.40 μg/mL) Cr^{3+} in water solution obeyed Beer's law (also see Fig. 5). The regression equation for the data being:

$$Y\ (\text{concentration; } \mu\text{g/mL}) = 0.1414x\ (\text{absorbance; } A) + 0.0011$$

The correlation coefficient square (R^2) was 0.9962, including the origin of coordinates (0.00, 0.00). This indicates that the Cr^{3+} concentration approaching 0.00 in water could be estimated by the regression equation mentioned above, depending on the sensitivity of the spectrophotometer used. This conclusion agrees with that (accurately detectable level <0.4 μg Cr^{3+}/mL) predicted by the regression model established by the test based on 0.4 – 2.0 μg Cr^{3+}/mL testing solutions in *Linear relationship between measurements by CCRS and concentration of Cr^{3+}*.

Since it was reported that dietary supplementation of Cr^{3+} at doses from 100 mg to 1000 mg per kg was not harmful,[32] this minimum detection level of CCRS is satisfactory for accurately determining Cr^{3+} for practical application.

Effect of other ions on the analytical reaction

It was found that such metal ions as Fe, Cu, Zn, Al, Zn, Ti, Ca, Co and Mg did not interfere in the determination method of Cr^{3+} reported in this paper. And also, the interference test indicated that Cr^{6+} did not react with chlorophosphonazo I to form a colored compound. This should indicate that the analytical method reported in this paper can accurately and rapidly determine Cr^{3+} with the presence of Cr^{6+}.

These results indicate that the specificity of the determination method of Cr^{3+} reported in this paper should be acceptable. Before drawing a comparison, the method based on the property of trivalent chromium to be a catalyst for the oxidation of Indigo Carmine with potassium periodate and to lose its color with the presence of ethylenediaminetetraacetic acid and sodium tripolyphosphate for measuring Cr^{3+},[29] may also need extensive study on the interference of variables.

Conclusions

The precision of both CCRS and AAS for the determination of the standard Cr^{3+} is identical and acceptable without the interference of Cr^{6+}. However, unlike CCRS, direct or selective determination of Cr^{3+} by AAS is difficult when Cr^{6+} is present in testing sample solutions. The percent recovery of added standard Cr^{3+} from natural mineral or pipe water by CCRS was 99.8 or 99.7, respectively.

The CCRS is accurate, reproducible and inexpensive. It also features reasonably good sensitivity and selectivity, and a high sample output. This first developed spectrophotometric method should be readily adapted for the routine and selective determination of Cr^{3+} in bottled mineral drinking water with (or without) the supplementation of Cr^{3+} or in natural water such as mineral or pipe water with the presence of Cr^{6+}. If total Cr content is measured, then the content of Cr^{6+} can be obtained by calculation.

On the basis of the procedure for determining Cr^{3+} developed in this study, large quantities of analysis per person per day can be very easily achieved if liquid dispensing systems or an automated system for the spectrophotometric measurements are used. Therefore, it is possible to widely apply this procedure in a routine analysis on a large scale.

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