



Research Article

Chromium Isotopes Detection in their Ores with Minimal Errors

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Abstract

The industrial production and use of chromium have grown considerably during the past five decades. Abundances of the chromium isotopes in terrestrial samples are identical to 0.01%. Among the dominant species of chromium, the trivalent form widely occurs in nature in chromite ores which is extremely immobilized especially in water bodies. Samples were mixtures of separated chromium isotopes and the calibration was made with the same species as those used in the measurements. The method had simplified the conversion of the ores to chromyl fluoride since the element could be readily separated as lead chromate from the leaching of chromite-sodium peroxide fusions. Isotope assay of chromyl fluoride under certain conditions was measured and the measurements of chromium isotopic anomalies ratios and isotope abundance of the chromite ores have been assessed. These provided sufficient quantitative mass spectrometric data, which were analyzed to calculate the abundance and the mean atomic mass of the questioned isotopes. Based on the high mass spectroscopy stability and the correction factors, the results were of good precision (incl. negligible systematic errors normally associated to inter-laboratory discrepancies) and the Cr isotopes availability ($^{52}\text{Cr} > ^{53}\text{Cr} > ^{50}\text{Cr} > ^{54}\text{Cr}$) was in conjunction with other classical tools such as oxygen isotopes. This paper is important for paleoecological, environmental, archeological, forensic, and nuclear researchers.

Introduction

Chromium is one of the elements on which no systematic study of the isotopic abundances has been made with regard to the geological source of the materials [1,2]. All the results of previously reported works were obtained with chemical reagents taken from the usual stores of these materials. As is evident in table 1, there is no real agreement among any of the results.

The main supply of chromium chemicals available in many countries, is from the chromite deposits [7,8]. Thus, it appears that the variation of the results listed in table 1, with the exception of those of Nowak [3], may be due to fractionation brought about in the chemical processing of the ores or by natural geological processes; or, they may be due to unknown discriminations involved in the various instruments with which the measurements were made.

Table 1: Previous determinations of the abundances of the chromium isotopes, in atoms percent.

Measurement Ion source reagent observer	1 Gas discharge Cr(CO) ₆ [3]	2 Thermionic Cr metal [4]	3 Electron impact CrCl ₃ [5]	4 Electron impact CrCl ₃ [6]
Isotope 50	4.9	4.49	4.31±0.04	4.41±0.06
Isotope 52	81.6	83.8	83.8±0.14	83.5±0.11
Isotope 53	10.4	9.55	9.55±0.09	9.54±0.06
Isotope 54	3.1	2.31	2.38±0.02	2.61±0.09

With this in mind, a study was made of the abundances of the Cr isotopes in samples of chromite and other chromium bearing minerals collected from well-characterized deposits. The present paper reports the results of the initial studies dealing with the primary mineral, chromite. Descriptions are given of the precautions taken to eliminate instrumental discriminations and the development of a technique by which highly precise measurements can be made with this and the other transition elements. A report of the studies on secondary chromium minerals will be given in a subsequent publication.

Materials and Methods

Materials

Survey of the chromite sources production in the world

Table 2 lists eighteen chromite specimens obtained from countries responsible for 81% of the chromite ore produced from 1931 to 2018 [9-22].

Methods

Strategy: In a previous publication [23] a preparation of chromyl fluoride (CrO_2F_2) by vacuum distillation from a solid-solid mixture of chromium trioxide (CrO_3), and cobalt (iii) fluoride (CoF_3), was described. The high vapor pressure of chromyl fluoride and its convenient preparation made this compound ideal as a means of introducing the element into the mass spectrometer (MS) as a gas, which affords the experimenter the advantage of extremely stable sample conditions. To avoid any possibility of introducing errors due to the possible isotopic effects on the fragmentation of this compound, CrO_2F_2^+ ions were chosen as the ion currents on which to base each abundance determination [24]. The anisotopic nature of fluorine simplified the handling of the MS data.

Analytical protocols: Since considerable chemical manipulation is required to convert chromite ores $(\text{Fe, Mg})\text{Cr}_2\text{O}_4$ to CrO_3 , a simpler procedure for preparing CrO_2F_2 was sought. In the course of this search, experiments revealed that the CrO_3 used in the above method could be replaced by lead chromate (PbCrO_4). This greatly simplified the conversion of the ores to chromyl fluoride, since the element could be readily separated as lead chromate from the leaching of chromite ($\text{Cr}_2\text{O}_4^{2-}$)-sodium

Table 2: Source and type of chromite used in the study.

Ore number	Location of deposit	Remarks	References
1	Tiebaghi, New Caledonia	Red ore	[9]
2	Fantoche, New Caledonia	Grey ore	[9]
3	Acoje or Zambales, Philippines		[10]
4	Rustenberg, Western Transvaal		[11]
5	Lydenberg, Eastern Transvaal		[11]
6	Western Transvaal	Exact location unspecified	[11]
7	Transvaal		[11]
8	Rhodesia	Great Dyke, 190 miles NNE of Selukwe, concentrates from alluvial deposits	[12]
9	Rhodesia	Great Dyke, 150 miles NNE of Selukwe, friable lump	[12]
10	Elazig Province, Turkey	Guleman ore from near Erganimaden	[13]
11	Ural Mountains, Russia	Russian chrome, several possible locations	[14,15]
12	Angelita, Cuba	Concentrates of Holquin ore	[16,17]
13	Black Lake, Quebec	Recent operation	[18]
14	Black Lake, Quebec	Concentrates	[18]
15	Black Lake, Quebec	Old sample from early operations at Black Lake	[18]
16	Hartford County, Maryland	Near Cooktown	[19]
17	Texas, Pennsylvania		[20]
18	Benbow, Montana	Concentrate	[21,22]

peroxide (Na_2O_2) fusions. To accomplish this, the ores were finely pulverized, fused with an excess of sodium peroxide, and leached with distilled water. The leaching was neutralized with glacial acetic acid, filtered to remove the silica, and then solid lead acetate was added to precipitate the chromium as lead chromate. Excess reagents were used throughout to ensure complete separation of the chromium, thus avoiding any possible isotopic fractionation effects during chemical treatment. The lead chromate was filtered, washed, air dried, and then ignited at from 400 to 500°C [25,26] to remove any residual organic matter as well as to dry the material. The ignited lead chromate was immediately transferred into a dry box through the route revealed in figure 1, where it was stored until used.

For conversion to chromyl fluoride the lead chromate was finely ground and intimately mixed with an excess of CoF_3 . The mixture was placed in a copper reaction tube. Bronze turnings were placed above the charge to prevent blow-over of the reactants during subsequent evacuation of the reaction tube.

The reaction tube was removed from the dry box and attached to the remainder of the sample preparation apparatus. The assembled sample preparation apparatus consisted of a 0.25 in. copper reaction tube which was about 6 in. long, a 0.25 in. copper U-tube, and a packless, bellows-type valve (Hoke M482). The components were joined by means of standard flare fittings, and the assembled apparatus was attached to the inlet system of the mass spectrometer through a stainless steel fitting (Hoke S24). An aluminum gasket was used to make the latter connection vacuum tight.

MS preparation method: A furnace was placed about the reaction tube and the temperature was raised to 375°C. This initial heat served to outgas the reactants and reaction tube without any loss of chromyl fluoride since the fluorination reaction does not proceed at this temperature. The outgassing was accompanied by an increase of pressure which was monitored by the inlet vacuum system Pirani gauge. When the pressure had returned to near normal, a dry-ice-trichloroethylene (C_2HCl_3) slush was placed about the U-tube to trap the chromyl fluoride, and the furnace temperature was increased to 550°C. Again the pressure in the inlet vacuum system increased due to oxygen produced during the fluorination of the lead chromate. When the pressure had returned to normal, the reaction was considered complete. The furnace was removed, and the chromyl fluoride was then treated like any other condensable gas. Samples of this compound could be stored in the copper container for several days without any apparent deterioration.

MS optimization method: The mass spectrometer employed in the study was a 180° instrument of 5 in. radius (Consolidated Electrodynamics Corporation, Model 21-220, modified in our laboratory). A 200 μA current of 70 V electrons ionized the chromyl fluoride at an analyzer pressure of less than 5×10^{-7} mm Hg, indicated by an ionization gauge placed within 12 in. of the ion source. The vacuum system was arranged to give differential pumping. Preliminary experiments to determine the optimum instrumental operating conditions were performed using a reference sample

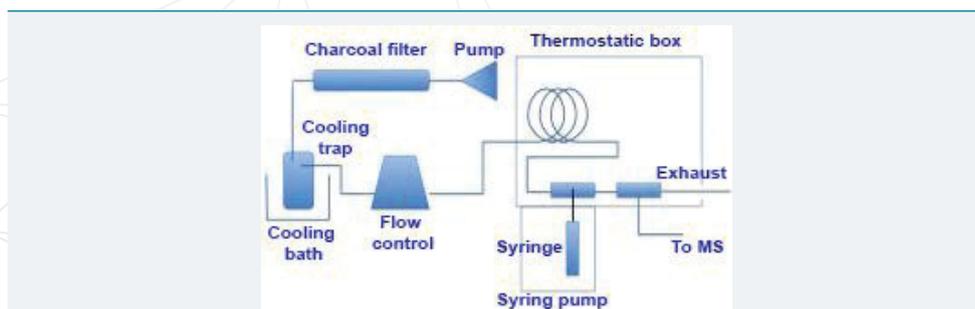


Figure 1: Schematic view of the novel direct aqueous injection system.

of chromyl fluoride prepared from lead chromate, which had been prepared from reagent-grade chromic bromide (Br_3Cr). This chromyl fluoride was assayed over the complete mass range of the instrument and found to be 99+ percent pure with the principal impurity being HF.

Results and Discussion

MS optimization outcomes

Preliminary experiments showed that the sensitivity of the MS for the CrO_2F_2^+ ions was constant in the ion accelerating voltage range of from 1600 to 1700 V. This meant that the isotopic CrO_2F_2^+ ion currents could be voltage scanned in that range, which was more convenient than magnetic scanning. It was found that the most reproducible results were achieved when the CrO_2F_2^+ ions were manually scanned to obtain the desired mass spectrograms. Ten spectrograms were made by scanning the mass region 120-124 in alternate directions. Consecutive spectrograms were averaged, which resulted in nine sets of data for each assay of any particular chromyl fluoride sample.

Oxygen isotopes intervention and their correction

The oxygen isotopes could not be ignored in any isotope determination using CrO_2F_2^+ ions, since ion currents at masses 121, 125 and 126 were observed and their magnitudes agreed with those calculated for ions containing ^{17}O and ^{18}O .

Since direct measurement of the oxygen isotopes in CrO_2F_2 was not possible, an indirect measurement was made. Given that the production of chromyl fluoride involved the fluorination of PbCrO_4 by means of CoF_3 , some means of examining directly the abundance of the oxygen isotopes in this chromate was sought. The most direct procedure developed involved the reaction of lead chromate with potassium fluobromite, KBrF_4 [26,27].

The liberated molecular oxygen was introduced directly into a dual collector, 60°, 6 in. radius mass spectrometer and the $^{34}\text{O}_2/^{32}\text{O}_2$ and $^{33}\text{O}_2/^{32}\text{O}_2$ ratios measured. Atmospheric oxygen, for which Nier [4] and Young et al. [28] gave an absolute ratio for $^{34}\text{O}_2/^{32}\text{O}_2$ of 0.00409, was used as a comparison standard in order to place all measurements on an absolute basis.

All of the PbCrO_4 samples prepared from the ores listed in table 2 and the distilled water were examined. The results of the KBrF_4 fluorinations along with that of CoF_3 are summarized in table 3.

From these results, it appeared that the oxygen in the PbCrO_4 was derived primarily from the distilled water used to leach the sodium peroxide-chromite fusions and to wash the precipitated lead chromate. To ensure that, fractionation of the oxygen isotopes did not occur during the fluorinations. One experiment was performed in which four different samples of O_2 were collected at various times during the reaction. Assay of this gas gave identical results with those already cited.

An exchange experiment designed to confirm the nature of the exchange between CrO_4^{2-} and H_2O^8 was performed. Vacuum-dried sodium chromate was dissolved in water enriched in ^{18}O to 5 atom percent. As soon as complete solution was achieved, the water was distilled off and crystalline Na_2CrO_4 recovered.

After being dried under vacuum at 70°C for 7 hr, this material was fluorinated with KBrF_4 . (In this case the fluorination proceeded smoothly at 200°C.) Measurement of

Table 3: KBrF_4 and CoF_3 fluorination reactions.

Item	Reaction	$^{33}\text{O}_2/^{32}\text{O}_2$	$^{34}\text{O}_2/^{32}\text{O}_2$
1	$\text{PbCrO}_4 + \text{KBrF}_4 \xrightarrow{400^\circ\text{C}} \text{O}_2 + \dots$	0.000730 ± 5	0.003930 ± 5
2	$\text{H}_2\text{O} + \text{KBrF}_4 \xrightarrow{25^\circ\text{C}} \text{O}_2 + \dots$	0.000730 ± 5	0.003930 ± 5
3	$\text{PbCrO}_4 + \text{CoF}_3 \xrightarrow{550^\circ\text{C}} \text{O}_2 + \dots$	0.000730 ± 5	0.003930 ± 5

the $^{34}\text{O}_2/^{32}\text{O}_2$ ratio for the evolved oxygen indicated complete exchange within the short time of the experiment. This is essentially in agreement with the results of Brodskii and Dontsova [29] and of Mills [30] whose measurements of the oxygen isotopes were based on the density of the water employed. On the basis of these results, it was concluded that correction of the observed CrO_2F_2^+ ion currents for the oxygen isotopes had to be based upon the observed abundances in the distilled water. Accordingly, corrections of the observed ion currents were made on the basis of $^{16}\text{O}/^{17}\text{O} = 2740$, and $^{16}\text{O}/^{18}\text{O} = 508.9$ for the oxygen isotopes in the distilled water and the assumption that the oxygen in chromyl fluoride was a random collection of oxygen atoms.

Thus, the calculated abundances of the ^{16}O , ^{16}O ; ^{16}O , ^{17}O ; and ^{16}O , ^{18}O combinations were 99.536, 0.073, and 0.391 percent, respectively. Any other combinations were present to less than 0.001 percent and were considered negligible.

The equations which relate the observed ion currents to the abundances of the chromium isotopes are:

$$^{120}\text{M} = ^{50}\text{A} \quad (1)$$

$$^{122}\text{M} - 0.00393 ^{50}\text{A} = ^{52}\text{A} \quad (2)$$

$$^{123}\text{M} - 0.00073 ^{52}\text{A} = ^{53}\text{A} \quad (3)$$

$$^{124}\text{M} - 0.00073 ^{53}\text{A} - 0.00393 ^{52}\text{A} = ^{54}\text{A} \quad (4)$$

Where M is the observed ion current, A is the relative abundance, and the superscript is the isotopic mass number. The factors 0.00073 and 0.00393 are the ratios ^{16}O , $^{17}\text{O}/^{16}\text{O}$, ^{16}O and ^{16}O , $^{18}\text{O}/^{16}\text{O}$, ^{16}O , respectively. A simplification which introduced negligible error was the replacement of the terms ^{52}A and ^{53}A in the left hand members of the equations (3) and (4) with ^{122}M and ^{123}M , because the products of the decimal fractions involved were negligible. Thus equations (1) to (4) were reduced to:

$$^{122}\text{M} - 0.00393 ^{120}\text{A} = ^{52}\text{A} \quad (5)$$

$$^{123}\text{M} - 0.00073 ^{122}\text{A} = ^{53}\text{A} \quad (6)$$

$$^{124}\text{M} - 0.00073 ^{123}\text{A} - 0.00393 ^{122}\text{A} = ^{54}\text{A} \quad (7)$$

These were used in all the subsequent treatment of the data.

Experimental pressure effect

Since there was small probability of obtaining equal ion currents for all eighteen samples of chromyl fluoride, the reference sample of chromyl fluoride was assayed at one-half, at normal, and at twice the normal operating pressure to determine whether or not the assays were pressure dependent. The results of this experiment are shown in table 4. They indicate that no pressure effect on the assays occurred and that the electrometer tube input resistor was truly ohmic in its behavior.

Comparative inter-laboratory study

Comparison of the assays of the chromyl fluoride prepared from the eighteen chromite ores depended on the stability of the instrument during the period required to assay the materials and the absence of any fractionation effects during the production of the CrO_2F_2 and its subsequent volatilization into the inlet system of the

Table 4: Isotope assay of chromyl fluoride at various pressures (Isotope abundance, atoms percent).

Isotope	50	52	53	54
Half normal pressure	4.335	83.768	9.529	2.368
Normal pressure	4.332	83.759	9.535	2.373
Twice normal pressure	4.343	83.760	9.524	2.372

mass spectrometer. Accordingly, three different check experiments were devised. The first check involved chromyl fluoride made from commercial CrO_3 and assayed four different times during a 12 day period. The second and third checks involved different chromyl fluoride preparations from lead chromate which had been made from reagent-grade chromic bromide. In the second check, two samples of chromyl fluoride, made from different portions of the lead chromate, were assayed 5 days apart. In the third check, an additional preparation was assayed four times during a 5 day period. Thus, all fractionation or discrimination possibilities were considered. The average assay and single standard deviation of each check are shown in table 5 in columns A, B and C, respectively. These results indicated that comparison of the assays of the eighteen ore samples could be made with no concern about day-to-day instrumental drift or chemical fractionation effects.

Analytical challenges

Another potential error involved the exact nature of gas flow in the mass spectrometer. The sample inlet system of the instrument was equipped with a viscous leak which consisted of a 5 in. length of copper capillary tubing of 0.005 in. internal diameter terminated by an adjustable constriction. Differential pumping in the ion source indicated the probability that mass discrimination due to effusive flow was present. However, it has been shown that the nature of the correction factor that should be applied to isotope measurements for this and other instrumental discriminations is dependent upon the detailed physical conditions existing in a particular mass spectrometer [31,32]. It is therefore most reliable to determine these correction factors by calibration of the instrument by means of mixtures of separated isotopes.

Mixtures of separated chromium isotopes were first considered for this calibration. Thus the calibration would have been made with the same species as those used in the measurements. Attempts to use CrO_2F_2 prepared from mixtures of these materials were fruitless due to an inability to assay the separated isotopic materials satisfactorily with the instrument at hand. This was principally the result of an exchange between the chromium of the chromyl fluoride and the chromium of the Nichrome V (9–21% Cr, 2.5% Mn (max), 1.0% Fe (max), 0.75–1.6% Si, 0.15% C (max), balance Ni) used in the construction of the ion source. This exchange resulted in assay errors whose magnitude depended on the difference of the sample composition from that of normal chromium.

Overcoming solutions

For samples whose isotopic abundances were normal, errors from this effect were computed to be negligible. The difficulty might have been circumvented by constructing a new source of some other material or gold plating the existing source. Both of these possibilities were considered and the latter was seriously contemplated. This will be done for the extension of the work to secondary chromium materials where the preliminary experiments indicate differences in the isotopic constitution.

Suggested corrective measures: A compromise calibration for the present phase of the work was accomplished with a mixture of separated nitrogen isotopes which was carefully prepared and assayed according to the method described by Junk and Svec [33] to produce absolute abundance values. This mixture was then assayed with

Table 5: Instrument stability (Isotope abundance, atoms percent).

Mass	A	B	C
50	4.347 ± 0.005	4.353 ± 0.005	4.347 ± 0.003
52	83.754 ± 0.016	83.760 ± 0.008	83.760 ± 0.005
53	9.515 ± 0.009	9.515 ± 0.007	9.521 ± 0.005
54	2.384 ± 0.005	2.372 ± 0.003	2.372 ± 0.004

Variations cited are standard deviations.

the mass spectrometer employed throughout the chromium tests under conditions in which the range of ion acceleration voltage was as nearly identical as possible with those under which the chromium assays were made. The value obtained here for the nitrogen isotope mixtures was 42.29 atom percent ^{15}N compared to 42.18 obtained by Junk and Svec [33]. However, the indicated agreement to one part in 423 was obtained only when the data were corrected for fractionation due to effusive gas flow from the ion source. A correction factor equal to the square root of the inverse ratio of the masses involved had to be applied. Because the precision obtained in this calibration approached that obtained with the chromium measurements, it was safe to assume that all of the mass discrimination due to gas flow could be considered to be the result of effusion of the sample material from the ion source.

After these preliminary experiments, the samples of chromyl fluoride prepared from the eighteen chromite ores were assayed along with the reference sample during a 2 week period. The observed data for the ores were first corrected for gas flow discrimination and then for the oxygen isotope effect. The results are listed in tables 6,7. Table 6 gives the individual assays of the eighteen samples and the average assay. Table 7 gives the standard deviation associated with each individual assay and the average of the eighteen individual standard deviations.

Comparison of the results listed in tables 6,7, shows that the standard deviation from the average assay of the eighteen ores was nearly identical to the average standard deviation associated with each individual assay. It must therefore be concluded that there is no variation in the isotopic composition of chromium with respect to the source of chromite ore. In order to examine the statistics of the determinations further, every individual datum from each of the assays was grouped into a composite of 170 items for each isotope abundance.

The standard deviation of the composite data (Table 8) is larger but is more reliable than that of the average assay of the eighteen ores, because in the calculation of the latter, the standard deviation for each individual assay was ignored.

Despite the good precision of the data above, it was necessary to consider whether or not the values obtained represented the absolute abundances of the chromium isotopes and were not merely relative values. The results of the previously mentioned

Table 6: Isotope abundance determination of the chromite ores (Isotope abundance, atoms percent).

Isotopes Samples	50	52	53	54
1	4.357	83.763	9.497	2.373
2	4.348	83.774	9.506	2.371
3	4.357	83.757	9.506	2.379
4	4.350	83.748	9.522	2.380
5	4.351	83.764	9.511	2.374
6	4.347	83.781	9.505	2.368
7	4.348	83.771	9.510	2.371
8	4.357	83.750	9.496	2.388
9	4.357	83.764	9.500	2.379
10	4.353	83.754	9.515	2.378
11	4.346	83.769	9.509	2.377
12	4.348	83.759	9.514	2.379
13	4.346	83.762	9.515	2.377
14	4.352	83.764	9.509	2.374
15	4.347	83.759	9.519	2.376
16	4.348	83.767	9.512	2.373
17	4.352	83.771	9.508	2.369
18	4.362	83.767	9.502	2.369
Ave.	4.352	83.764	9.509	2.375
SD	0.004	0.008	0.007	0.005

Table 7: Standard deviation associated with each abundance determination of the chromite ores shown in Table 6 (Standard deviation x 1000).

Isotopes Samples	50	52	53	54
1	10.1	8.80	5.30	4.70
2	3.80	6.70	5.00	3.10
3	9.40	10.9	12.5	4.00
4	2.60	6.00	4.60	2.30
5	4.80	9.00	3.90	3.50
6	4.20	10.2	4.20	4.50
7	2.60	5.50	5.60	3.40
8	5.70	9.60	4.20	3.90
9	3.30	6.00	3.20	2.90
10	2.40	3.80	3.60	2.00
11	5.70	7.90	4.40	3.80
12	3.10	7.30	2.60	3.50
13	10.5	11.6	5.60	3.70
14	2.10	6.70	5.30	4.50
15	2.40	13.6	13.8	3.60
16	3.50	9.70	8.50	3.10
17	3.80	8.10	3.70	5.00
18	10.3	14.7	7.20	3.40
Ave.	5.00	8.70	5.70	3.60

Table 8: Composite of all data for chromite ores.

Mass	Abundance (%)	± Standard deviation	Number of items outside 3 σ limit
50	4.352	0.008	2
52	83.764	0.012	0
53	9.509	0.009	0
54	2.375	0.006	1

experiments, which were designed to measure and correct for discrimination effects due to gas flow, voltage scanning, variation in gas pressure, non-ohmic electrometer input resistors, impure sample gases, and instrumental drift, led the writers to assume that the resulting measurements were absolute.

Conclusion

Using the available literature, chromite ores gathered from various deposits throughout the world were assayed for the abundances of the chromium isotopes. However, no differences in the relative abundances were observed.

Upon application of criteria to determine the absoluteness of the measured abundances of the isotopes of chromium, the only discrimination observed during the measurements was that due to effusive gas flow out of the ionizing region of the ion source. The magnitude of this discrimination was determined from measurements of a mixture of separated nitrogen isotopes and corrections were made for it. On this basis, the abundances of the chromium isotopes reported in this communication can be considered absolute. Since chemical chromium has a common source, it is conservative to accept these absolute abundance values for the isotopes in reagent chromium. At the $\pm 3\sigma$ level (99.7% confidence level), the recommended values in atoms percent are:

$$\text{Cr}^{50} = 4.352 \pm 0.024$$

$$\text{Cr}^{52} = 83.764 \pm 0.036$$

$$\text{Cr}^{53} = 9.509 \pm 0.027$$

$$\text{Cr}^{54} = 2.375 \pm 0.018$$

Using these values and the previously published and accepted values for the masses of the chromium isotopes [34,35], a value for the chemical atomic weight (conversion factor = 1.000275) of 51.998 ± 0.001 has been obtained wherein the stated uncertainty combines the effects of both mass and abundance measurements and is computed by conventional statistical methods.

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