Original Paper

Determination of coloring elements in the glass raw materials limestone and dolomite by flame atomic absorption spectrometry

Report of the International Commission on Glass (ICG) Technical Committee 2 "Chemical Durability and Analysis"

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A method is described for the determination of impurities such as iron, chromium, manganese, nickel, cobalt and copper in the glass raw materials limestone and dolomite. The proposed method involves the direct measurement technique in aqueous solution by flame atomic absorption spectrometry. It has been proved to be an accurate and quick method for analyzing concentrations normally found in these raw materials.

Bestimmung der färbenden Elemente in den Glasrohstoffen Kalkstein und Dolomit durch Flammen-Atomabsorptionsspektrometrie

Es wird ein Verfahren zur Bestimmung von Verunreinigungen wie Eisen, Chrom, Mangan, Nickel, Kobalt und Kupfer in den Glasrohstoffen Kalkstein und Dolomit beschrieben. Bei der vorgeschlagenen Methode handelt es sich um ein direktes Meßverfahren in wäßriger Lösung mit der Flammen-Atomabsorptionsspektrometrie. Es hat sich als eine genaue und schnelle Möglichkeit zum Analysieren der normalerweise in diesen Rohstoffen vorkommenden Konzentrationen erwiesen.

1. Introduction

Almost all commercially produced flint glasses contain some amount of oxides of the transition metals (titanium to copper) which impart color to glass, the hue and intensity of which depending upon the kind and the valence state of the ion, its total concentration and the respective concentrations of its different valence states in the glass composition. In most cases, the amount of such oxides is very small and they do not produce a distinct color. However, this may nevertheless be detrimental to some glass types (such as high-quality tableware) since it reduces the brightness of the product. The transition metal oxides are mostly transferred to glass as impurities from raw materials. Therefore, it is a usual practice to limit their amount in the raw materials.

Technical Committee 2 (TC2 "Chemical Durability and Analysis") of the International Commission on Glass (ICG) developed and published a method for the determination of low impurity amounts of e.g. sodium, potassium, magnesium, calcium, aluminum, iron, chromium and titanium in glassmaking sands [1]. During this investigation, TC2 was also interested in establishing a method for the analysis of coloring elements such as iron, chromium, copper, nickel, cobalt and manganese in limestone and dolomite. There is a number of national standards and excess of reports in the technical literature describing different procedures for analyzing limestone and dolomite, many of which are well-known and widely used [2 to 5]. However, they describe procedures for the major components, such as CaO and MgO etc., which are of interest in calculating batch compositions, but they do not cover all the coloring elements under investigation here. For example, iron, chromium and manganese are determined only by conventional methods that are tedious and time-consuming.

In TC2, in a general discussion held on this subject, all members agreed to provide their in-house procedures and for a report on the ranges of coloring elements in various glassmaking limestones and dolomites. The evaluation of the data concerning typical compositions of the German, Turkish, Chinese, UK and USA limestones and dolomites revealed that the method which was to be established should be able to determine chromium, cobalt, nickel and copper as low as 1 mg/kg and manganese and iron up to 1000 mg/kg. Four proposals based on the measurement by flame atomic absorption spectrometry (FAAS) and one proposal by inductively

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Table 1. Sieve analysis results (in wt%) of different limestone and dolomite samples, taken from the bottom, middle and upper regions of raw material sacks

grain size in mm	limestone no. 10		limestone no. 11		dolomites A and B		
	upper	bottom	upper	bottom	upper	middle	bottom
>1.0	38.0	58.7 1)	=	–	trace	trace	trace
0.5 to 1.0	30.0	29.1	trace	trace	trace	trace	trace
0.315 to 0.5	13.8	7.8	0.1	0.2	trace	trace	trace
0.2 to 0.315	8.4	2.5	0.4	0.5	trace	trace	trace
0.1 to 0.2	8.2	1.4 2)	4.3	4.1	trace	trace	trace
0.071 to 0.1	0.8	0.2	6.5	4.8	trace	trace	trace
<0.071	0.8	0.3	88.7	90.4	100	100	100

1) Analysis on fraction >1.0 mm for: Fe = 280 mg/kg, Cu = <1 mg/kg.
2) Analysis on fraction 0.1 to 0.2 mm for: Fe = 441 mg/kg, Cu = 2.4 mg/kg.

coupled plasma emission spectrometry (ICP) were discussed in detail. In the former technique, the sample measuring solution is prepared by two methods. The first one utilizes solvent extraction separation and preconcentration (pyrolidine dithiocarbamate and diethyldithiocarbamate chelates are used with methyl isobutyl ketone as solvent), whereas the second method involves direct measurement of the coloring elements with background correction in aqueous solution. FAAS based on direct measurement has proved to be a quick and accurate method for determining concentrations of the afore-mentioned elements normally found in the glass raw materials limestone and dolomite. The results provided by TC2 members who have ICP in their laboratories are also included in the collaborative studies in order to show an alternative.

TC2 started this work in 1987 with two sets of samples: the limestones no. 10 and 11 and the dolomites A and B (from Schott Glaswerke, Mainz (Germany)). The dolomites seemed to be homogeneous. Limestones no. 10 and 11 were not homogeneous enough due to segregation, which probably occurred during the transportation. Later, the limestones were replaced with new ones whose homogeneities were tested and found to be acceptable. The work on the determination of coloring elements in dolomite and limestone was completed in April 1995.

2. Preliminary investigations

2.1 Testing homogeneity

The variation of the particle size distribution throughout the stocks of limestones no. 10 and 11 and dolomites A and B was investigated at Schott Glaswerke to examine the possibility of segregation which may occur during transportation. The results given in table 1 indicate that the dolomites are free from segregation and assumed to have the same impurity content throughout the stock. However, for the limestones, especially limestone no. 10, a certain difference in particle size distribution has been detected between the upper and lower parts of the stock. This has been further supported by chemical analysis of the fine and coarse fractions. For this reason, TC2 did no more work on limestones no. 10 and 11.

Table 2. Investigation on Fe, Cr, Cu contents (in mg/kg) in limestone distributed by Sekurit St. Gobain (Germany) using in-house procedures

laboratory no.	Cr	Fe	Cu
1	8.9	711	<1
6	4.1	714	<1
7	6.6	658	3.2
9	2.7	609	<1

A new limestone stock was supplied by the laboratory of Sekurit St. Gobain, Aachen (Germany). To check its homogeneity, four laboratories carried out a new investigation. The results displayed in table 2 showed a great scattering. In order to clarify whether this was due to the different analysis techniques employed or to the inhomogeneity of the stock, an exchange of samples was carried out between laboratories no. 6 and 7 and laboratories no. 1 and 9, respectively. The fresh results attained imply that the limestone stock seemed to be homogeneous and the scattering of the results was to some extent probably due to the different analysis methods (table 3).

2.2 Method of analysis and results

At the TC2 meetings, the in-house methods and reports in the technical literature were evaluated in detail. Finally, the proposals from Pilkington plc, Lathom (UK), received closer attention. The Pilkington laboratory was asked to carry out experimental work on the reference dolomite-BCS 368 by the direct measurement technique with background correction and the solvent extraction technique using FAAS (table 4). The values obtained by both methods agreed well with each other and also with the certified values. The TC2 members found it more suitable to use the direct measurement technique with background correction since it was less time-consuming and produced almost the same values as the solvent extraction technique.

Under the light of the discussions, it was decided to organize a collaborative investigation on the dolomites A and B and the new limestone which had been proved to be homogeneous. The results are tabulated in tables 5 to 7. It was also accepted to analyze these three samples

Table 3. Investigation on Cr, Fe, Mn, Cu contents (in mg/kg) in limestone. Results obtained by laboratories no. 6 and 9 on their own samples and on samples of laboratories no. 7 and 1.

		results in laboratory no. 6		results in laboratory no. 9	
		own sample	sample of laboratoty no. 7	own sample	sample of laboratoty no. 1
Cr	content in mg/kg	4.1	4.0	2.7	3.4
Fe		714	690	609	630
Mn		88	82	n. d.	n. d.
Cu		<1	<1	<1	<1

n.d. = not determined.

Table 4. Comparison of direct measurement and solvent extraction techniques carried out on reference dolomite-BCS 368 at Pilkington plc (UK)

	trace element data (certified values)				content in mg/kg	
	$\bar{X}$ in mg/kg	S_R	l	t	direct measurement by FAAS	solvent extraction and measurement by FAAS
Cr	39	4	8	3	36	40
Cu	3	1	7	1	3	3
Co	no value				1	1
Ni	<5	–	10	3	<1	1
V	no value				<2	<2

Explanations: $\bar{X}$ = overall mean value, S_R = coefficient of reproducibility, l = number of laboratories, t = number of techniques.

Table 5. Investigation of impurity contents (in mg/kg) in limestone with the first working draft and in-house methods by MAS

laboratory no.	Fe content			Cr content			Ni content			Mn content			Cu content			Co content		
	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s
first working draft of analysis method																		
2	3	597	±31		n. d.		3	3.9	±0.2	3	58	±1.3	3	4.3	±0.3	3	4.6	±0.2
4	2	702	±15	2	5.0	±0.2		n. d.		2	88	±1.0	2	4.7	±1.0	1	0.5	
6	2	675	± 4		n. d.			n. d.		2	61	±0.5		n.d.			n.d.	
7	2	617	± 6	2	2.7	±0.2	2	4.0	±0.3	2	54	±0.5	2	1.2	±0.1	2	1.2	±0.1
9	3	697	± 4	3	<10		3	3.2	±0.2	3	81	±0.2	3	<2		3	<2	
MAS results																		
4	2	684	±11	2	4.0	±0.2				1	75							
7	2	665	± 5															
9	2	464	± 3	2	5	±0.0				2	85	±1.0						

Explanations: n.d. = not determined, n = number of element determinations in each laboratory, $\bar{x}$ = mean value in each laboratory, s = standard deviation in each laboratory.

Table 6. Investigation of impurity contents (in mg/kg) in dolomite A with the first working draft, solvent extraction technique and in-house methods by MAS

laboratory no.	Fe content			Cr content			Ni content			Mn content			Cu content			Co content		
	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s
first working draft of analysis method																		
2	3	2520	±24		n.d.		3	6.5	±0.3	3	451	±2	3	6.9	±0.5	3	3.2	±0.5
4	2	2705	±35	2	8.8	±1.0		n.d.		2	523	±3	2	10.1	±0.9	1	0.2	
7	2	2540	± 8	2	4.2	±0.1	2	4.5	±0.1	2	454	±2	2	4.4	±0.3	2	1.0	±0.1
9	3	2764	±19	3	<10		3	5.7	±0.2	3	461	±2	3	4.2	±0.2	3	<2	
solvent extraction technique																		
6	3	2750	±11	3	4.6	±0.2	2	4.4	±0.2	2	472	±4	3	4.5	±0.1	3	1.5	±0.1
MAS results																		
4	2	2700	±10	2	6.9	±0.4				1	472							
7	2	2565																
9	2	2412	± 4	2	5.0	±0.0				2	460	±1						

Explanations: n.d. = not determined, n = number of determinations in each laboratory, $\bar{x}$ = mean value in each laboratory, s = standard deviation in each laboratory.

Table 7. Investigation of impurity contents (in mg/kg) in dolomite B with the first working draft, solvent extraction technique and in-house methods by MAS

laboratory no.	Fe content			Cr content			Ni content			Mn content			Cu content			Co content		
	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s
first working draft of analysis method																		
2	3	1523	± 5		n.d.		3	3.8	±0.4	3	502	±5.0	3	6.5	±0.6	3	4.0	±0.7
4	2	1640	±32	2	3.7	±0.2		–		2	572	±5.0	2	9.2	±1.1	1	1.0	
7	2	1459	± 1	2	1.8	±0.1	2	2.1	±0.2	2	509	±5.0	2	4.5	±0.3	2	2.0	±0.2
9	3	1655	±15	3	<10		3	3.2	±0.2	3	524	±4.9	3	4.0	±0.0	3	<2	
solvent extraction technique																		
6	3	1555	± 7	3	3.3	±0.1	3	2.0	±0.1	3	544	±0.8	3	4.5	±0.1	3	2.4	±0.1
MAS results																		
4	2	1650	±10	2	3.2	±0.2				1	520							
7	2	1500																
9	2	1530	±11	2	3.5	±0.5				2	512	±8.5						

Explanations: n.d. = not determined, n = number of determinations in each laboratory, $\bar{x}$ = mean value in each laboratory, s = standard deviation in each laboratory.

Table 8. Investigation of impurity contents (in µg of element per ml of solution) in limestone solutions A and B; solution A = normal, solution B = enriched with the analyzed elements by artificial addition

laboratory no.	content (in µg/ml) in solution A						content (in µg/ml) in solution B					
	Fe	Cr	Mn	Cu	Co	Ni	Fe	Cr	Mn	Cu	Co	Ni
1	29	0.12	3.0	0.08	0.07	0.09	108	0.33	21	0.18	0.20	0.16
2	31	1.18	2.3	0.08	0.28	0.33	138	1.99	24	0.24	0.52	0.47
4	37	0.28	4.6	0.13	0.22	0.19	137	0.52	30	0.28	0.35	0.32
6	35	0.11	4.3	0.09	0.07	0.17	145	0.35	31	0.25	0.28	0.41
7	29	0.12	3.8	0.09	0.05	0.19	124	0.29	56	0.19	0.22	0.31
8	37	0.18	4.4	0.02	0.73	0.81	145	0.36	30	0.14	0.90	0.96
9	35	0.60	4.1	0.06	0.05	0.14	140	1.29	31	0.21	0.98	0.33
12	31	0.18	3.3	0.06	0.13	0.15	117	0.40	25	0.20	0.29	0.29

Table 9. Statistical evaluation of the results attained on limestone solutions A and B

	solution A						solution B					
	Fe	Cr	Mn	Cu	Co	Ni	Fe	Cr	Mn	Cu	Co	Ni
$\bar{X}$	33	0.17	3.7	0.08	0.06	0.16	135.1	0.38	27.4	0.21	0.31	0.36
CV	10.0	39.2	21.3	28.2	19.2	24.4	7.9	21.2	14.7	21.1	37.4	19.7
S_R	3.31	0.06	0.80	0.02	0.01	0.04	10.7	0.08	4.04	0.04	0.12	0.07
l	8	8	8	8	8	8	8	8	8	8	8	8
L	8	6	8	7	4	6	7	6	7	8	6	6

Explanations: $\bar{X}$ = overall mean value in µg/ml, CV = coefficient of variance, S_R = coefficient of reproducibility, l = total number of laboratories, L = accepted number of laboratories.

Table 10. Investigation of impurity contents (in µg of element per ml of solution) in the sample solutions; solution A: normal attack on limestone, solution B: "reagents" only, solution C: attack on pure $CaCO_3$

laboratory no.	content (in µg/ml) in solution A						content (in µg/ml) in solution B						content (in µg/ml) in solution C					
	Fe	Cr	Mn	Cu	Co	Ni	Fe	Cr	Mn	Cu	Co	Ni	Fe	Cr	Mn	Cu	Co	Ni
2	32.2	0.17	4.2	0.05	0.16	0.14	0.16	0.02	0.02	0.02	0.09	0.08	0.17	0.04	0.09	0.03	0.16	0.14
4	31.5	0.07	3.1	0.02	0.04	0.13	0.07	n. d.	<0.01	<0.01	<0.01	0.04	0.07	n.d.	0.02	<0.01	<0.01	0.05
6	35.2	0.11	3.7	0.10	0.05	0.13	0.23	<0.02	n.d.	<0.03	<0.03	<0.03	0.18	<0.02	0.04	<0.03	<0.03	<0.03
7	35.0	0.17	2.9	0.04	0.11	0.22	0.26	<0.02	0.04	<0.03	<0.03	<0.03	0.59	0.05	0.08	0.02	0.09	0.13
9	33.8	0.75	3.9	0.02	0.06	0.12	0.12	0.10	<0.02	<0.02	0.04	<0.02	0.20	0.45	0.07	0.02	0.04	0.04

n.d. = not detected.

Table 11. Final results of the determination of impurity contents (in mg/kg) in limestone with the recommended procedure (calculated according to ISO 5725 [12])

laboratory no.	Fe content in mg/kg			Cr content in mg/kg			Ni content in mg/kg			Mn content in mg/kg			Cu content in mg/kg			Co content in mg/kg		
	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s
recommended procedure																		
2	3	9.9	±0.4	3	0.8	±0.1	3	2.0	±0.1	3	5.2	±0.1	3	0.8	±0.2	3	2.7	±0.6
4	3	9.7	±1.5	3	<2		3	<1		3	4.7	±1.5	3	1.6	±0.6	3	<1	
5	3	13.0	±1.7	3	2.0	±0.0	3	<1		3	5.0	±0.0	3	<1		3	<2	
6	3	8.7	±0.3	3	1.7	±0.0	3	<2		3	4.1	±0.4	3	3.5[3]	±0.4	3	<2	
7	3	14.0	±0.5	3	2.0	±0.3	3	<2		3	4.6	±0.2	3	<2		3	<2	
9	3	12.3	±0.3	3	<2		3	<2		3	5.2	±0.0	3	<2		3	<2	
12	3	19.0[3]	±1.0	3	2.0	±0.0	3	2.0	±0.0	3	5.0	±0.0	3	1.0	±0.0	3	3.0	±0.0
plasma method[4]																		
5					2.2			2.7										
6		<8			0.6			<2			2.4			2.9			<2	
11		8.8			0.7			n.d.			5.3			0.5			n.d.	
16	3	11.0	±0.1	3	1.7	±0.1	3	1.8	±0.0	3	4.5	±0.1	3	0.9	±0.0	3	1.0	±0.1

Explanations: n = number of determinations in each laboratory, $\bar{x}$ = mean value in each laboratory, s = standard deviation in each laboratory. n.d. = not detected.
[3] Outlier. [4] Not included in statistical evaluation in table 12.

only for their chromium, iron and manganese contents by Molecular Absorption Spectrometry (MAS) using in-house methods. A statistical evaluation did not make sense because only five laboratories took part. However, the results seemed to be not very satisfactory. The probable sources of error such as background correction, interference by neighboring lines or by the mass of the present ions and possibly still poor homogeneity of the stocks were discussed in detail.

To clarify these points, it was decided to carry out experimental work on the limestone solutions prepared by the Institut National du Verre, ASBL, Charleroi (Belgium). The results are displayed in table 8. Solutions A and B contained the same non-analyzed ions (i.e. CaO, MgO, etc.) in identical concentrations. For the ions to be analyzed, the differences in their concentrations were created by the enrichment of one of the solutions by artificial addition by the said ions. This means that the ions which could cause interference and should be eliminated by background correction are therefore the same in both solutions. As it is seen from table 8, there are several analytical and/or apparatus problems in some laboratories. This is also apparent in the statistical evaluation of the results given in table 9.

Another set of three new solutions was prepared by the Institut National du Verre, ASBL:

- solution A: normal attack on the same limestone according to the proposed procedure;
- solution B: "reagents" only;
- solution C: attack on pure $CaCO_3$ to see the matrix effect of calcium.

Before the investigation was carried out, the participating laboratories were asked to check their background correction efficiency and take other necessary precautions. The comparison of the results is given in table 10. Only five laboratories took part and one laboratory declared in advance to have background correction problems. Two groups of results were recognized as produced by laboratories no. 2, 7 and laboratory no. 4, 6 and 9, respectively, but the differences between them, except for iron in laboratory no. 7 and chromium in laboratory no. 9 are not very large, being of the same order of magnitude as the analytical error. Once again, it was confirmed that the background correction is essential to obtain accurate results. However, even under carefully controlled operating conditions, some discrepancies due to matrix effects could occur.

Table 12. Statistical evaluation of the results attained for iron and manganese in table 11

	Fe	Mn
overall mean value, $\bar{X}$, in mg/kg	11.3	4.8
coefficient of repeatablility, S_r	0.8	0.3
coefficient of reproducibility, S_R	1.9	0.4
coefficient of variance, CV	17.1	8.3
total number of laboratories, l	7	7
accepted number of laboratories, L	6	7
total number of determinations, n	21	21
accepted number of determinations, N	18	21

2.3 Final procedure and results

During the TC 2 meetings, all the problems encountered in applying the just described procedure were discussed. These were the effects of background correction, flame conditions, the amount of reagents and fusion salts and the use of multielement calibration solutions. Finally the recommended procedure was established. With this procedure, the results on the fresh limestone and dolomite samples as shown in tables 11 to 14 are achieved. The homogeneity of the new stocks was checked in terms of iron, manganese and chromium by X-ray fluorescence spectrometry by the laboratory of St. Gobain Recherche.

Table 13. Final results of the determination of impurity contents (in mg/kg) in dolomite with the recommended procedure (calculated according to ISO 5725 [12])

laboratory no.	Fe content in mg/kg			Cr content in mg/kg			Ni content in mg/kg			Mn content in mg/kg			Cu content in mg/kg			Co content in mg/kg		
	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s
recommended procedure																		
2	3	1135	±22	3	2.9	±0.2	3	2.5	±0.4	3	327	±1	3	0.8	±0.1	3	2.2	±0.3
4	3	985	± 5	3	4.1	±0.2	3	1.4	±0.3	3	303	±3	3	2.4	±0.9	3	<1	
5	3	1182	± 5	3	5.7[3)]	±0.3	3	<1		3	309	±2	3	<1		3	2	±0.0
6	3	1182	±16	2	4.1	±1.7	3	2.3	±0.7	3	303	±3	3	<2		3	<2	
7	3	1090	± 9	3	3.1	±0.5	3	2.5	±0.1	3	290	±3	3	4.2[3)]	±1.9	3	<2	
9	3	1324	±74	3	4.6	±0.3	3	2.5	±0.1	3	299	±3	3	<2		3	<2	
12	3	1162	± 7	3	3.9	±0.2	3	3.1	±0.2	3	282	±1	3	0.8	±0.1	3	<1	
plasma method[5)]																		
1	3	1170	±26	3	3.7	±0.5		<10		3	290	±4	3	1.2	±0.5		<2	
5					4.0			0.4										

Explanations: n = number of determinations in each laboratory, $\bar{x}$ = mean value in each laboratory, s = standard deviation in each laboratory. [3)] Outlier. [5)] Not included in statistical evaluation in table 14.

Table 14. Statistical evaluation of the results attained for iron, chromium and manganese in table 13

	Fe	Cr	Mn
overall mean value, $\bar{X}$, in mg/kg	1151	3.8	302
coefficient of repeatablility, S_r	19.7	0.5	2.3
coefficient of reproducibility, S_R	95	0.6	13.2
coefficient of variance, CV	8.3	15.8	4.4
total number of laboratories, I	7	7	7
accepted number of laboratories, L	7	6	7
total number of determinations, n	21	21	21
accepted number of determinations, N	21	18	21

Ten laboratories took part in this collaborative investigation and satisfactory results were achieved. The results attained for limestone indicate that the coefficient of variation, *CV*, is somewhat higher for iron and very good for manganese. Chromium, nickel, cobalt and copper levels are near the detection limits (tables 11 and 12). The repeatability for iron in laboratory no. 12 and for copper in laboratory no. 6 may partly be due to sample inhomogeneity and partly to laboratory contamination. As for the dolomite results tabulated in tables 13 and 14, they reveal that *CV*s for iron and manganese are very good. The *CV* for chromium is a litte high, but this is quite acceptable at such impurity concentration level. Nickel, copper and cobalt values are near the detection limits. Higher values attained for chromium in laboratory no. 5 and for copper in laboratory no. 7 can be attributed to the above-mentioned reasons given for limestone. The plasma results reported by some laboratories agree with the overall mean values achieved for the coloring ions under investigation. In general, it can be concluded that for these levels of impurity concentrations, the procedure works well.

3. Principle of the method

The sample is decomposed with hydrochloric acid and the insoluble matter separated by filtration. The filter paper containing the insoluble matter is ignited and treated with hydrofluoric and sulfuric acids. The residue is fused in sodium carbonate and boric acid and the cold melt dissolved in hydrochloric acid. The sample and standard solutions are aspirated into the flame of the atomic absorption spectrometer under specified conditions. Background correction is applied to each element.

3.1 Definitions

A large number of terms used in atomic absorption spectrometry are defined in [6], but, for convenience, the definitions of the more frequently used terms in this report are as follows:

- Analyte: element to be determined.
- Stock solution: solution containing the analyte, usually expressed as its oxide, in known but high concentration.
- Standard solution: solution containing the analyte, expressed as its oxide, in known concentration suitable for the preparation of calibration solutions.
- Set of calibration solutions: set of simple or combined reference solutions having different, but known analyte concentrations. The zero member is the solution containing no analyte but all of the additives.
- Optimum working range: range of concentrations of an analyte in solution over which the relationship between absorbance and concentration is linear.
- Sample solution: solution, which is produced by dissolving the decomposed limestone/dolomite and made up to a defined volume.
- Sample measuring solution: solution, which is used for the final measurements for calculation of the results (= SS), may be the sample solution or its dilution.

3.2 Reagents

Water complying with the requirements of grade 2 or better in [7] and superpurity ("Aristar" grade) reagents, i.e., better than analytical grade, shall be used throughout unless otherwise stated. Commercially available element standard solutions for spectrometry may be used in the preparation of reference solutions. Dilutions e.g. (1+1) refer to 1 volume of the concentrated reagent of the original solution being diluted by 1 volume of water. The reagents are:

- sodium carbonate, Na_2CO_3 ("Aristar" grade),
- boric acid, H_3BO_3 ("Aristar" grade),
- hydrochloric acid, HCl (specific gravity (sp. gr.) 1.18) ("Aristar" grade), (1+1), (1+12), (1+99),
- hydrofluoric acid, H_2F_2, 40 % m/m ("Aristar" grade),
- sulfuric acid, H_2SO_4, (sp. gr. 1.84) ("Aristar" grade), (1+1).
- Potassium chromate (K_2CrO_4)
  For chromium stock solution dissolve 3.735 g of potassium chromate in water and dilute to 1 l with water: 1 ml = 1 000 µg Cr.
- Metallic cobalt
  For cobalt stock solution dissolve 1.0000 g of cobalt metal in a minimum volume of (1+1) HCl. Dilute to 1 l with (1+99) HCl: 1 ml = 1 000 µg Co.
- Metallic copper
  For copper stock solution dissolve 1.0000 g of copper metal in a minimum volume of (1+1) HCl. Dilute to 1 l with (1+99) HCl: 1 ml = 1 000 µg Cu.
- Metallic iron (wire)
  For iron stock solution dissolve 1.0000 g of iron wire in a minimum volume of (1+1) HCl. Dilute to 1 l with (1+99) HCl: 1 ml = 1 000 µg Fe.
- Metallic manganese
  For manganese stock solution dissolve 1.0000 g of manganese in a minimum volume of (1+1) HCl. Dilute to 1 l with (1+99) HCl: 1 ml = 1 000 µg Mn.
- Metallic nickel
  For nickel stock solution dissolve 1.0000 g of nickel in a minimum volume of (1+1) HCl. Dilute to 1 l with (1+99) HCl: 1 ml = 1 000 µg Ni.

3.3 Apparatus

Ordinary laboratory apparatus and usual laboratory glassware, made from borosilicate glass 3.3 [8], comply with the requirements of relevant international standards. New containers (beakers, volumetric flasks, storing bottles, etc.) should be treated before use by filling to 90 % of the overflow volume with hydrochloric acid (1+12) and heated for 2 h at boiling, for example in a liquid bath. The containers should then be rinsed with water, filled with water to 90 % of the overflow volume and heated as above for two periods of 1 h, using fresh water each time.

Furthermore, there are used as apparatus:

- A flame atomic absorption spectrometer, equipped with line sources for iron, chromium, copper, cobalt, nickel, and manganese and with gas suppliers and burners for air/propane, air/acetylene and nitrous oxide/acetylene mixtures.
- An analytical balance (accurate to 0.1 mg or better).
- A 10 ml burette (graduated 0.02 ml) complying with the requirements of class A in [9].
- Microburettes, of suitable capacities to measure the volumes required in table 16 (section 3.4.3).
- Pipettes, of suitable capacities complying with the requirements of class A [10].
- Platinum crucibles, of suitable capacity, with lid.
- Beakers, of suitable capacities.
- Volumetric flasks of suitable capacities complying with the requirements of class A [11].
- Mortar and pestle, agate.
- Water bath.
- Hot plate.

3.4 Preparation of standard solutions and calibration solutions

3.4.1 Single-element standard solutions

Dilute the stock solutions by means of pipettes according to table 15.

3.4.2 Multielement standard solution

Transfer the volumes of stock solutions shown in column 2, aliquot of table 15 to a 1 000 ml volumetric flask, add 10 ml of hydrochloric acid (sp. gr. 1.18), dilute to the mark and mix. This solution contains the elements added in the concentrations shown in column 5 of table 15.

3.4.3 Set of calibration solutions

Prepare the set of single-element calibration solutions from the standard solutions or the set of multielement

Table 15. Preparation of single-element standard solutions from stock solutions

element	aliquot in ml	addition of HCl (sp.gr.1.18) in ml	final volume in ml	element concentration in µg/ml
Cr	5	10	1000	5
Co	5	10	1000	5
Cu	5	10	1000	5
Fe	20	10	1000	20
Mn	20	10	1000	20
Ni	5	10	1000	5

Table 16. Example of the preparation of a set of single or multi-element calibration solutions

element to be measured	standard solution in ml					
	0	1	2	3	5	10
	concentration of the element in 50 ml of single or multi-element calibration solution in µg/ml					
Cr	0	0.1	0.2	0.3	0.5	1.0
Co	0	0.1	0.2	0.3	0.5	1.0
Cu	0	0.1	0.2	0.3	0.5	1.0
Fe	0	0.4	0.8	1.2	2.0	4.0
Mn	0	0.4	0.8	1.2	2.0	4.0
Ni	0	0.1	0.2	0.3	0.5	1.0

calibration solutions to suit the quality of the limestone and/or dolomite being analyzed. Table 16 shows the preparation of a set of calibration solutions. All calibration solutions should contain 5 ml of hydrochloric acid (sp. gr. 1.18) per 50 ml, i.e. 10 % v/v, respectively.

Note: No significant interelement effect was noted using multielement calibration solutions; and also no matrix effect in case of real sample matrixes under the conditions described by the procedure.

3.5 Sample preparation

Spread the finely ground (<100 µm) sample of limestone or dolomite in a thin layer on a clean piece of polythene sheet and obtain a sample of approximately 10 g by taking increments with a plastic spatula. Dry for 1 h at 110 °C, allow to cool and store in a stoppered sample bottle in a desiccator.

3.5.1 Preparation of the sample solution

Weigh two approximately 2.5 g portions (to the nearest 0.1 mg) of the dried, finely ground sample into separate tall form beakers. Add 40 ml water, 10 ml hydrochloric acid (1+1), cover the beaker with a clock glass and warm on a boiling water bath. Transfer to the hot plate and boil for 10 min.

Cool the solution and filter through a close filter paper to remove any undissolved particulate matter. Reserve the filtrate and transfer the filter to a clean platinum crucible. Dry the filter in an oven at 110 °C, and ignite gently until all the carbon has been removed.

Moisten the contents of the cold crucible with water, add 2 to 3 drops of diluted sulfuric acid (1+1) and about 5 ml of hydrofluoric acid. Evaporate to dryness and continue to heating for 5 min.

Fuse the residue from the hydrofluoric acid treatment with 1 g of sodium carbonate and 0.5 g of boric acid. Extract the fused mass with 12 ml hydrochloric acid (1+1) and add back to the filtrate. Evaporate the solution to give a final volume of 45 ml, cool and dilute to 50 ml in a volumetric flask with water.

3.5.2 Preparation of the blank solution

A reagent blank is prepared by using the same procedure but omitting the sample.

Table 17. Elements with absorbance lines and flame gases

element	absorbance line in nm	flame gas
Cr[6]	357.9	N_2O/C_2H_2
Co	240.7	air/C_2H_2
Cu	324.7	air/C_2H_2
Fe	248.3	air/C_2H_2
Mn	279.5	air/C_2H_2
Ni	232.0	air/C_2H_2

[6] 3-slot burner and single-element hollow cathode lamp(HCL) instead of multi-element HCL increase the sensivity and stabilize the readings. They might be preferred for measurement. In case of 3-slot burner, as flame gases, air/C_2H_2 is used.

3.5.3 Measurement of the metal concentration

The lampcurrent, monochromator slit-width and burner oxidant/fuel ratio are adjusted to give maximum sensitivity. The sample and standard solutions are aspirated into the flame of the atomic absorption instrument according to the manufacturer's instructions. Background correction is applied to each element by the use of a deuterium or tungsten correction source.

The absorbances are noted for each solution. Recommended absorbance lines and gas mixtures for the elements under investigation are as summarized in table 17.

3.6 Calculation

A graph of absorbance versus concentration is plotted and the concentration of the analyte in the sample solution is read from the calibration graph. The concentration of the analyte in the sample (in mg/kg) is calculated from the following relationship:

$$X = \frac{(R_S - R_{BL}) \cdot V \cdot D}{W}$$

with X = concentration of analyte in the sample in mg/kg, R_S = readout for the element in the sample measuring solution in µg/ml, R_{BL} = readout for the element in the blank test solution (BS) in µg/ml, V = volume of the sample solution in ml, D = dilution factor, W = weight of the sample in g.

*

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[10] International standard ISO 648: Laboratory glassware; one-mark pipettes. Geneva: ISO, 1977.
[11] International standard ISO 1042: Laboratory glassware; one-mark volumetric flasks. Geneva: ISO, 1983.
[12] International standard ISO 5725: Precision of test methods; determination of repeatability and reproducibility for a standard test method by inter-laboratory tests. Geneva: ISO, 1986.

5. Appendix

The following members of Technical Committee 2 of ICG participated in the described round robin for the determination of coloring elements in the glass raw materials limestone and dolomite:

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