Original Paper

Spectrophotometric analysis of ferrous, ferric and total iron content in soda–lime–silica glass

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A study of the bands of charge transfer and of d–d transition was performed in view of quantitative analysis of ferrous, ferric and total iron content. For a given wavelength between 0.32 und 0.33 μm a linear relationship between the absorption and the total iron content can be found for all the redox states studied. Using the band at 1.06 μm allows [Fe^{2+}] determination and by means of the band at 0.38 μm [Fe^{3+}] can also be measured accurately if correction is made using the total iron content. The results of spectroscopic determinations are shown to be coherent with those of chemical analysis to within 1 to 3 %.

Spektrofotometrische Analyse des Fe^{2+}-, Fe^{3+}- und Gesamteisengehaltes in Kalk-Natronsilicatglas

Eine Untersuchung der Banden der Ladungsübertragung und des d–d-Überganges wurde mit dem Ziel einer quantitativen Analyse des Fe^{2+}-, Fe^{3+}- und Gesamteisengehaltes durchgeführt. Für eine gegebene Wellenlänge zwischen 0,32 und 0,33 μm kann für alle untersuchten Redoxzustände eine lineare Beziehung zwischen der Absorption und dem Gesamteisengehalt gefunden werden. Die Verwendung der Bande bei 1,06 μm erlaubt die Bestimmung der Fe^{2+}-Konzentration. Mit Hilfe der Bande bei 0,38 μm kann auch der Fe^{3+}-Gehalt genau ermittelt werden, wenn eine Korrektur unter Anwendung des Gesamteisengehaltes durchgeführt wurde. Es konnte gezeigt werden, daß spektroskopische Messungen und chemische Analysen innerhalb von 1 bis 3 % übereinstimmen.

1. Introduction

The industrial production of coloured glass – particularly sheet glass – requires accurate control and perfect reproducibility of the colouring. The colour depends on the quantity of pigment oxides present and on their redox state which can alter during the manufacturing process [1 to 4]. It is therefore important to be able to analyze rapidly and, if possible, in situ, the levels of the metal ions responsible for the colouring. The present study focuses on iron oxide which is the most frequently used pigment and which is always present in glass either as an impurity or as an added pigment.

The total iron content can be determined by fluorescence (accuracy ≈ 3 %) or by emission spectroscopy (accuracy ≈ 5 %) but it is most often determined by atomic absorption (accuracy ≈ 2 %) after dissolving the glass. There are two techniques for Fe^{2+} assay which require the glass to be dissolved by acid attack under inert atmosphere [5 to 7]. In the solution obtained, the analysis can be performed by oxidoreduction with the help of ceric-sulphate solution or by spectrophotometry after complexation by 1,10-phenanthroline. In both cases, the accuracy is within 3 % but any possible alteration of the redox state during the attack is not taken into account. These destructive methods can obviously not be applied to in-line analysis of the glass as it is produced. Fe^{2+} can also be determined by spectrophotometry using the absorption band at 1.06 μm (claimed accuracy ≈ 3 %) [8 to 10]. This method has been applied to in-line use but the determination of the total iron content and of the redox ratio always rely on the use of the previous methods. There is, clearly, a call for a method allowing the simultaneous in-line measurement of the ferrous, ferric and total iron content.

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2. Basis of the method

The spectrophotometric method described in this work uses the linear relationship existing between spectral absorption factors and concentration both for Fe^{2+} and Fe^{3+} as well as for total iron. The originality of the method lies in the exploitation of the behaviour of the edges of charge-transfer bands in association with measurements of the absorption bands corresponding to the d–d transition usually used alone.

As demonstrated in the beginning of this section, there is a linear relationship, in certain conditions, between spectral absorption (as measured in certain specific conditions) and the total iron concentration. This relationship is shown in figure 1. The measurement was made at the edge of the charge-transfer absorption band. The absorption is thus easily measurable even though the molar extinction coefficient at the band peak is 100 to 1000 times higher than those of d–d bands which makes measurement at the peak of the band extremely difficult.

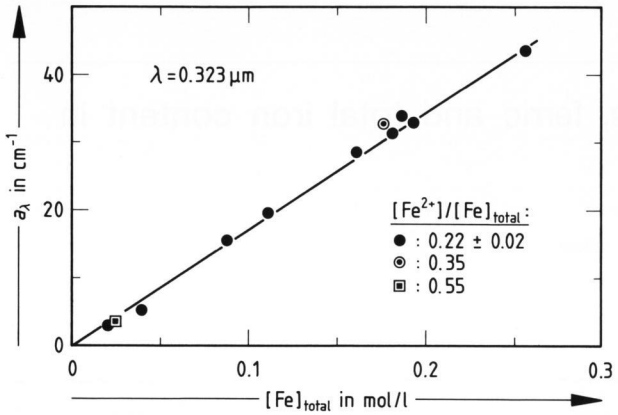


Figure 1. Variation of the absorption coefficient, a_λ, as a function of the total iron concentration of 11 glass samples with variable redox ratios $[Fe^{2+}]/[Fe]_{total}$ as parameters.

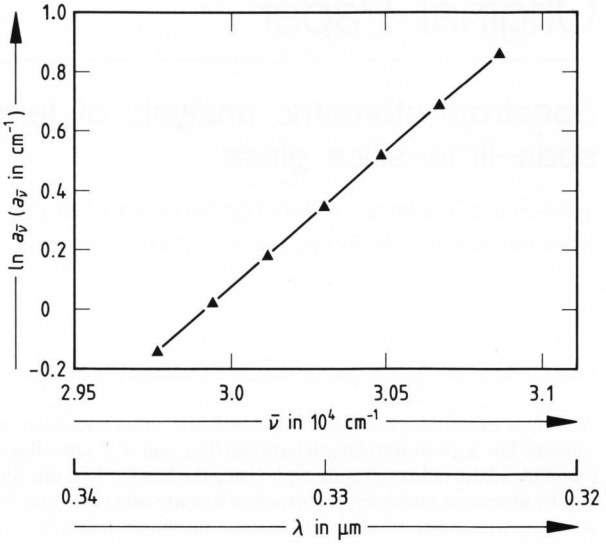


Figure 2. Example of variation of ln $a_{\bar{\nu}}$ as a function of the wave number $\bar{\nu}$ at the absorption edge for glass no. 1.

The Fe^{2+}- and Fe^{3+}-ion contents were determined in the usual way according to the Beer-Lambert's law from the absorption bands at 1.06 and 0.38 µm, respectively. The method benefits from the possibilities of deconvolution of the spectrum reported elsewhere [11]. Knowing the levels of iron, a correction can be made to the spectral absorption readings giving higher accuracy.

3. Analysis of soda–lime–silica glass containing iron

3.1. Experimental materials and basic scientific results

The composition (in mol%) of the vitreous matrix of the glass studied was as follows: 70.6 SiO_2, 13.4 Na_2O, 9.9 CaO, 5.9 MgO, 0.23 Al_2O_3, 0.05 TiO_2, 0.05 SO_3. The Fe_2O_3 content varied from 0.02 to 0.25 mol/l and the redox ratio from 0.19 to 0.55 (table 1).

3.1.1. Charge-transfer band analysis

The optical spectrum exhibits strong absorption bands at short wavelengths. The absorption-edge position depends on the colouring ion composition [11]. Moreover, the exponential variation of the a_λ absorption coefficient against the wavenumber ($\bar{\nu} = 1/\lambda$) was confirmed for values between around 0.8 and 5 cm^{-1}. Such a relationship can be found for any glass whatever the redox ratio may be. The corresponding linear variation of ln a_λ versus $\bar{\nu}$ is shown in figure 2 for glass no. 1. The relation can be expressed according to the equation:

$$\ln a_{\bar{\nu}} = p \cdot \bar{\nu} + q.$$

Validity is observed in a given wave number range as indicated in table 2 by the values of the minimum and maximum wave numbers. The parameter p is only slightly modified with the iron concentration, whereas the parameter q grows with it. This representation gives a set of approximately parallel straight lines indicating the shift of the absorption edge towards higher wavelengths.

Absorption coefficients can be calculated using this relationship and for a given wavelength between 0.32 and 0.33 µm an unexpected linear relationship between spectral absorption and the total iron concentration can be found for all the redox states ($[Fe^{2+}]/[Fe]_{total}$ between 0.19 and 0.55). The corresponding results appear in figure 1.

The authors succeeded in deconvoluting the charge-transfer bands into two Gaussian curves taking into account a slight linear background noise, notably due to the presence of intensive UV bands, characteristic of the vitreous matrix. These two curves are centered at 0.22 and 0.25 µm (figure 3).

Table 1. Ferrous, ferric and total iron concentration (in mol/l) and redox ratios of 12 investigated glasses (chemical analysis)

	glass no.											
	0	1	2	3	4	5	6	7	8	9	10	11
$[Fe^{2+}]$		0.00492	0.013	0.00754	0.0204	0.221	0.0347	0.0598[1])	0.0414	0.0384[1])	0.0375	0.0515
$[Fe^{3+}]$		0.0153	0.0107	0.0304	0.0648	0.0859	0.123	0.1109	0.138	0.142	0.153	0.202
$[Fe_{total}]$	$< 10^{-3}$	0.0202	0.0237	0.0379	0.0852	0.108	0.158	0.1707[2])	0.179	0.1804[2])	0.190	0.253
$[Fe^{2+}/Fe_{total}]$		0.244	0.549	0.199	0.239	0.205	0.220	0.350	0.231	0.213	0.197	0.204

[1]) Determined by spectrophotometry at 1.06 µm. [2]) Determined by X-ray fluorescence.

Table 2. Values of the parameters p and q of the 12 investigated glass samples (see table 1). $\bar{\nu}_{max}$ and $\bar{\nu}_{min}$ give the validity range of exponential approximation. $a_{\bar{\nu}\,max}$ and $a_{\bar{\nu}\,min}$ are the corresponding absorption coefficients

	glass no.											
	0	1	2	3	4	5	6	7	8	9	10	11
$p \cdot 10^4$ in cm	8.63	9.5	9.13	10	10.36	10.13	9.69	8.74	9.11	8.88	9.03	8.88
q	−28.3	−28.44	−27.10	−29.1	−29.38	−28.42	−26.69	−23.62	−24.8	−24.01	−24.5	−23.5
$\bar{\nu}_{max}$ in cm^{-1}	31 746	31 056	31 056	30 581	29 412	29 325	28 818	29 154	29 239	28 490	28 490	28 490
$\bar{\nu}_{min}$ in cm^{-1}	30 303	29 586	29 940	29 240	28 490	27 855	27 855	28 490	27 778	27 855	27 700	27 700
$a_{\bar{\nu}\,max}$ in cm^{-1}	0.405	2.89	3.51	4.41	3.00	3.67	3.42	6.41	6.34	3.64	3.5	5.00
$a_{\bar{\nu}\,min}$ in cm^{-1}	0.117	0.717	1.27	1.15	1.15	0.827	1.35	3.6	1.675	2.06	1.7	2.38

Taking into account the results obtained using this method on samples with variable redox conditions and after comparing them with the information contained in the literature, these bands were attributed to transitions between orbitals of oxygen ions and those of the ions Fe^{2+} and Fe^{3+} [11].

This interpretation is compatible with the exponential approximation previously presented [11]. Indeed, the absorption edge of the sum of two Gaussian functions with adjoining maxima can be closely estimated with a low margin of error by an exponential function. The relative position of the two bands also validates the linear relationship existing between the absorption coefficient at 0.32 μm and the total iron concentration.

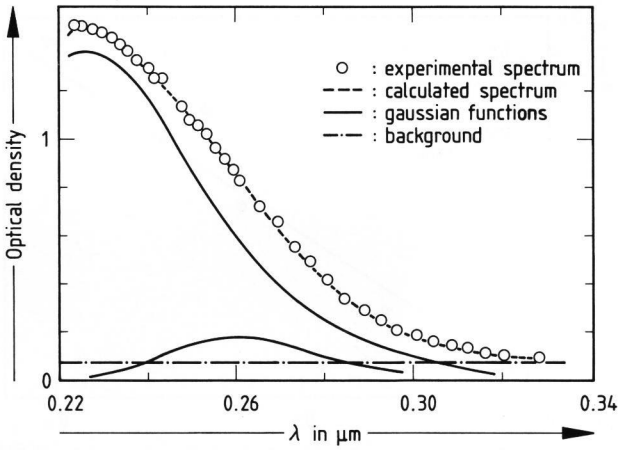


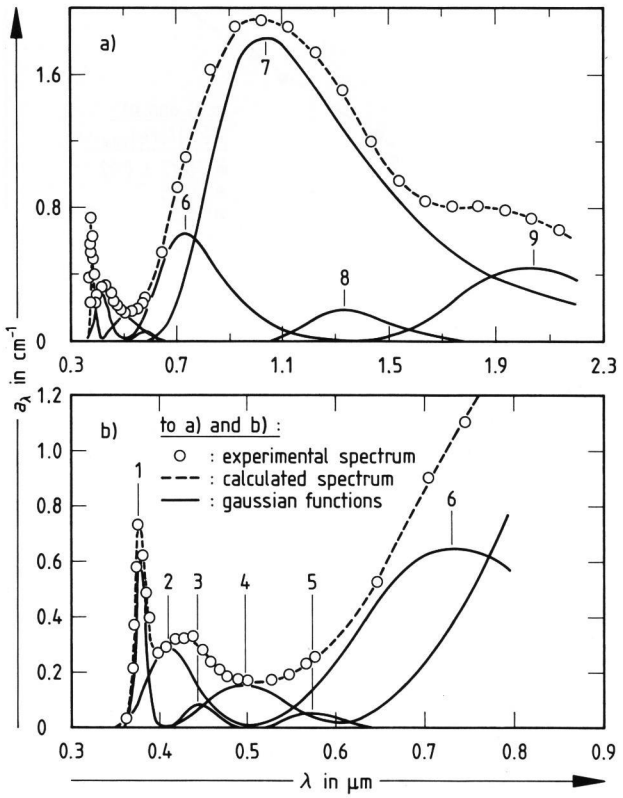
Figure 3. Deconvolution of the spectrum of the charge-transfer band for glass no. 6 after [11].

3.1.2. d→d iron transition band analysis

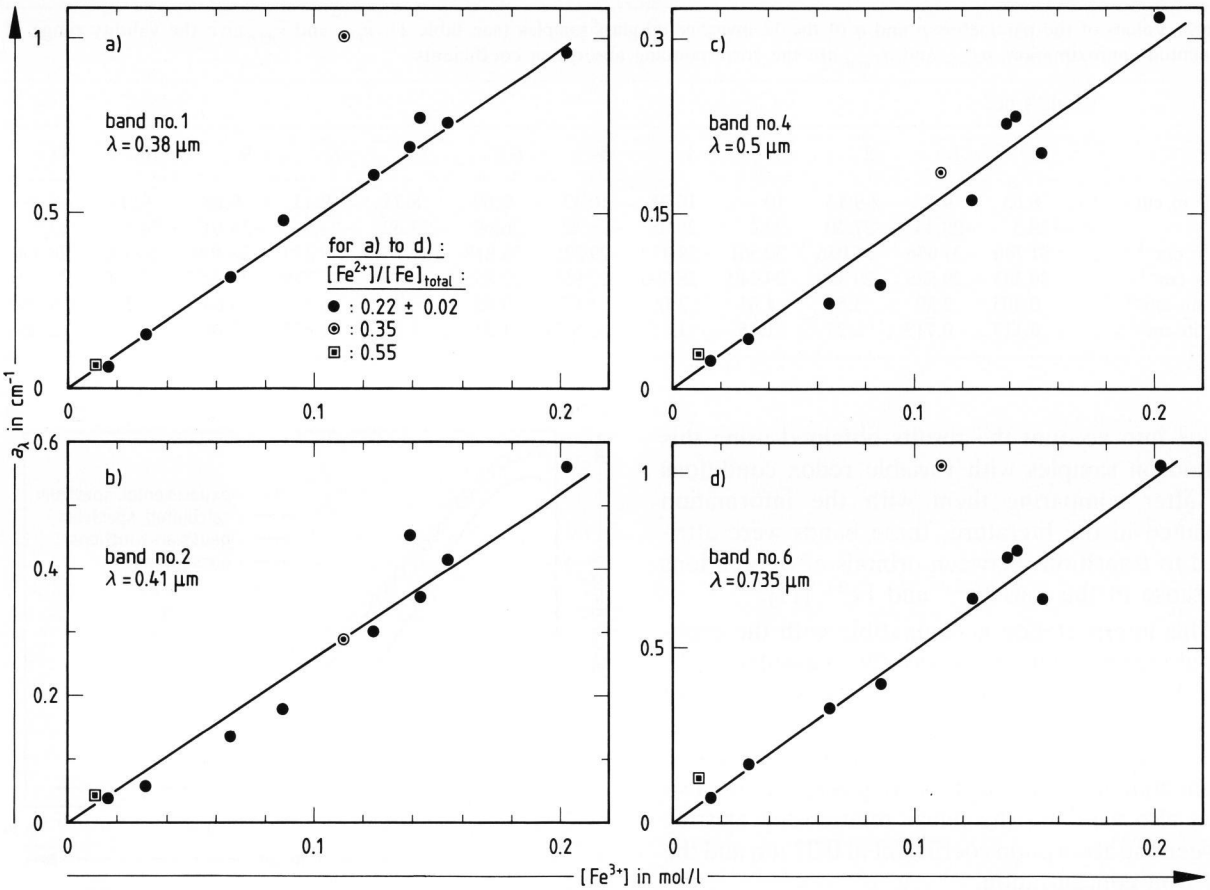
Ferrous and ferric ions can be in tetrahedral and/or octahedral surroundings. In a previous paper [11] the results of modelization of the spectrum using nine Gaussian functions as indicated in figures 4a and b were given. Bands no. 1 to 6 are attributed to Fe^{3+} transitions and bands no. 7 and 9 to Fe^{2+} transitions. The attribution of band no. 8 remains ambiguous. Variations of maximum intensities of the 8 bands identified were studied with respect to the concentration of the corresponding ions. A linear variation of the absorption coefficient is observed for bands no. 1, 2, 4, 6, 7 and 9 as shown in figures 5a to d and 6a and b. However, note that a discrepancy can occur concerning the Fe^{3+}-ion content in glass samples with redox ratio equal to 0.35. For the less intense bands no. 3 and 5 the dispersion is greater. From the linear relationships the extinction coefficients are calculated according to the Beer law and given in table 3.

3.2. Analytical procedure

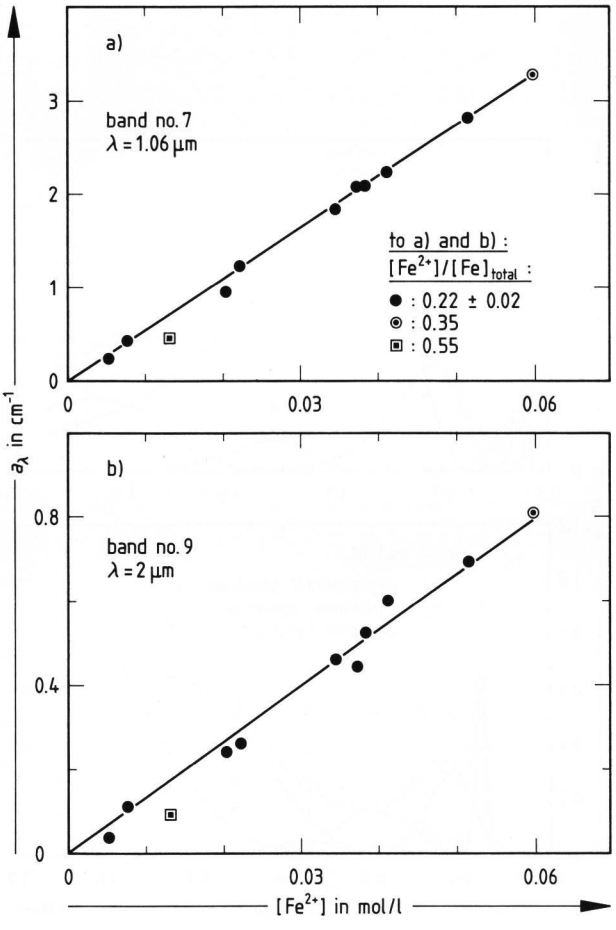
It is theoretically sufficient to determine the total iron content plus that of one of the two ions in which case



Figures 4a and b. Typical absorption spectra modeling for glass no. 6 after [11] with 9 Gaussian functions for the spectral zone of a) 0.3 to 2.3 μm, b) 0.3 to 0.9 μm.



Figures 5a to d. Variation of the absorption coefficient, a_λ, at the wavelength of the maximum absorption intensity due to d–d transition of the Fe^{3+} ion as a function of the Fe^{3+} concentration for glass samples with different redox ratios; a) band no. 1 at $\lambda = 0.38\ \mu m$, b) band no. 2 at $\lambda = 0.41\ \mu m$, c) band no. 4 at $\lambda = 0.5\ \mu m$, d) band no. 6 at $\lambda = 0.735\ \mu m$.



Figures 6a and b. Variation of the absorption coefficient, a_λ at the wavelength of the maximum absorption intensity due to d–transition of the Fe^{2+} ion as a function of the Fe^{2+} concentration for glass samples with different redox ratios; a) band no. 7 at $\lambda = 1.06\ \mu m$, b) band no. 9 at $\lambda = 2\ \mu m$.

the Fe^{2+} ion is chosen. However, the simultaneous determination of all three levels can increase the overall accuracy.

3.2.1. Determination of the total iron content

The edge of the charge-transfer band which was found to have an exponential-type relationship was used. The molar extinction coefficient at 31 000 cm^{-1} was 177 l/(mol cm). A preliminary calibration must be carried out. This must be performed on a series of samples containing various levels of iron between 0.01 and 0.8 wt% Fe_2O_3, i.e. within the range of industrially used concentrations.

It is first necessary to measure the absorption spectrum (0.31 to 0.39 μm depending on the pigment concentration). It is then possible to calculate the

Table 3. Extinction coefficient and wavelength at maximum absorption intensity for the 8 identified bands

	band no.							
	1	2	3	4	5	6	7	9
ion	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{2+}	Fe^{2+}
wavelength in μm	0.38	0.41	0.446	0.5	0.57	0.735	1.06	2
extinction coefficient in l/(mol cm)	4.857	2.556	0.975	1.391	0.751	4.927	53.845	12.9

relationship $\lg a_{\bar{\nu}} = p\,\bar{\nu} + q$ and to determine the values of p and q for each sample. As these standard samples had been analyzed chemically (atomic absorption) it was possible to plot $a_{\bar{\nu}}$ versus $[Fe]_{total}$ for a given wave number (figure 1). The wave number must be around 31 000 cm^{-1}. The absorption values used to take readings from the calibration curve were not experimental values but were calculated from the values of p and q. The accuracy of the readings was thus notably increased. As seen in figure 1, linearity is excellent and the accuracy of the determination can reach about 1 % ($\Delta[Fe]_{total}/[Fe]_{total}$).

3.2.2. Determination of the Fe^{2+} content

The authors used the d–d band at 1.06 μm which, as mentioned, had been used earlier in an analytical study [8 to 10]. This very wide band is in fact the envelope of bands no. 6, 7 and 8, but band no. 7 – attributed to a Fe^{2+} ion in an octahedral site – is preponderant. Beer's law remains roughly applicable for uncorrected experimental absorption readings. The dispersion of the molar extinction coefficient $\Delta\varepsilon/\varepsilon$ is then no greater than 10 %. This result can be improved by deconvoluting the spectrum using the absorption value corresponding to band no. 7. The dispersion is then about 5 %.

Spectrophotometric determination of the Fe^{2+} content at 1.06 μm can therefore be made with an accuracy of $\Delta[Fe^{2+}]/[Fe^{2+}]$ of 5 % using the absorption readings directly: An accuracy of about 3 % is obtained with a corrected spectrum and analysis should be made preferably for low redox ratio.

3.2.3. Determination of the Fe^{3+} content

The content of Fe^{3+} can, of course, be obtained from the difference between the levels of total iron and ferrous iron. Band no. 1 at 0.38 μm was used (attributed to a transition of Fe^{3+} in an octahedral site) but it is quite thin and is superimposed on the neighbouring bands. Application of Beer's law to the experimental readings of absorption gives a dispersion of the extinction coefficient $\Delta\varepsilon/\varepsilon$ of over 12 %. Modelling the spectrum lowers the dispersion which is reduced to 5 % using band no. 1. However, the level of the total iron content must be known to enable correction of the spectrum and analysis should be made preferably for low redox ratio.

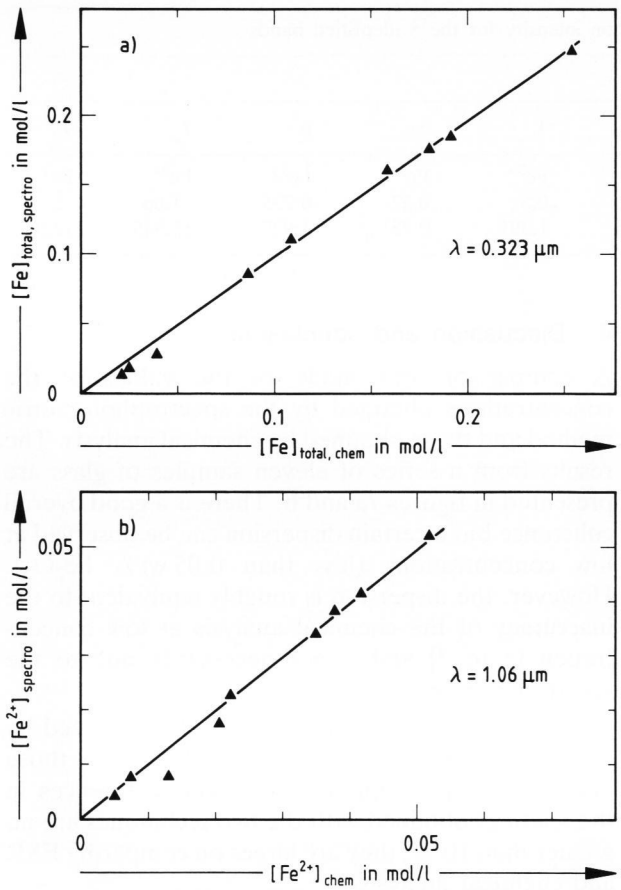
4. Discussion and conclusion

A comparison was made of the values of the concentrations obtained by the spectrophotometric method and those obtained by chemical analysis. The results from a series of eleven samples of glass are presented in figures 7a and b. There is a good overall coherence but a certain dispersion can be observed at low concentrations (less than 0.05 wt% Fe_2O_3). However, the dispersion is roughly equivalent to the inaccuracy of the chemical analysis at low concentration [5 to 7] and is not necessarily due to the spectrophotometric analysis.

The concentration of Fe^{2+} was also analyzed by ESR [12]. The results are concordant with those obtained by spectrophotometry. The differences in the readings obtained with the two techniques are no greater than 10 %; they are larger on comparing ESR and chemical analysis.

The implementation of the method relies on the simultaneous determination of the concentrations of total iron and of either Fe^{2+} or Fe^{3+}. The corresponding spectral absorption measurements must be made on glass in the shape of a sheet of known thickness with parallel faces, but such a determination can take benefit of the development of advanced spectrophotometry [13]. The values of $[Fe]_{total}$ and $[Fe^{3+}]$ can be obtained from the measurement of spectral absorption over the restricted range between 0.31 and 0.45 μm. From the spectrum, the values of the p and q parameters characteristic of the absorption edge, the corresponding value of absorption obtained by interpolation or by extrapolation to 0.32 μm and the corrected value of absorption attributed to Fe^{2+} at 0.38 μm are determined. With industrial application in mind, a simplification can be made by directly measuring spectral absorption at suitable wavelengths. The simultaneous determination of $[Fe]_{total}$ and $[Fe^{2+}]$ does, however, require analysis of two separate wavelength ranges. Industrial application is not any more complex for either of the methods.

The calibration values depend on the type of vitreous matrix studied. They should, therefore, usually be measured for each glass composition used. This might seem to represent a constraint limiting the range of application of the technique. However, the authors noted that small variations in composition had no influence on the values obtained on the



Figures 7a and b. Concentrations of iron in the glass samples studied obtained by spectrophotometry compared with those obtained by chemical analysis; a) $[Fe]_{total}$ at $\lambda = 0.323$ µm, b) $[Fe^{2+}]$ at $\lambda = 1.06$ µm.

condition that the matrix type remained the same. Since the composition only varies slightly in the case of industrial production, the range of application remains large. It will be necessary to establish a calibration curve for soda–lime–silica glass (sheet glass) and for the two types of borosilicate matrices (glass fiber and insulation glass).

The presence of oxide pigment other than iron oxide does not necessarily disturb the measurements. On the condition that they do not have charge-transfer bands in the same wavelength range, the results remain acceptable. This is, for example, the case of glass containing small amounts of cobalt oxide. Finally, if certain conditions are taken into account, the method can be extended to the determination of other pigment oxides which present a charge-transfer band in a suitable wavelength range.

The judicious use of the edges of charge-transfer absorption bands enables the accurate spectroscopic determination of the level of total iron contents in industrially-produced glass. Associating this determination with that, already used, of $[Fe^{2+}]$ gives a rapid and reliable measurement of the concentration and redox state of iron oxide. The findings can be confirmed by the determination of the Fe^{3+} content – also spectroscopically. This could possibly replace the determination of the Fe^{2+} concentration. However, a prerequisite for an accurate measurement is the correction of the absorption values using the total iron content.

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