The impact of refining agents on glass colour

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Idag har man mer och mer gått över från att luttra konstglas med arsenik till att använda antimon. Luttringsmedlet påverkar redoxnivån i glaset och därmed den färg man får vid jonfärgning. I den här undersökningen har vi studerat luttringsmedlen arsenik, antimon och cerium och vilken effekt de har på de färgande metallerna koppar, mangan, krom och järn. Vi har även färgat in glas utan luttringsmedel. Det visade sig att vid infärgning med koppar fås en starkare färg i glas luttrat med cerium än i de glas som är arsenik- eller antimonluttrade. En liknande effekt fås även i det manganfärgade glaset. Vid kromfärgning erhålls ett gulare glas vid arsenikluttring än vid antimonluttring och i det järnfärgade glaset blir ceriumglaset betydligt gulare än i glasen med antimon och arsenik.

Introduction

A conventional way of colouring glass is to introduce transition metals. These polyvalent ions colour the glass, see table 1 for some examples. The redox level of the glass will control the oxidation state of the metal ions and thus the colour of the glass. The refining agents used for crystal/handmade glass are also polyvalent ions and will have a large influence on the redox equilibrium in the melt. Arsenic oxide was in the past the dominating refining agent but nowadays antimony oxide is becoming a more and more frequently used alternative, especially in unleaded glass.

The refining agent used will influence the equilibrium of the colouring metal's ions. Xiang et al made a study where they investigated the influence of different metal ions on copper [1]. They suggested the following series of reducing power: Sb>As>Sn>Cu>Ce for a soda-lime silica glass. In this series antimony, arsenic and cerium are of interest as refining agents and the difference between antimony and cerium is proposed to be large. Antimony will reduce the copper while cerium will oxidise it, thus it is harder to colour an antimony refined glass with copper than a cerium refined glass. The reducing order for copper is thus investigated but no similar series are published for other colouring agents. We have made an extended correlation between the refining agent and the colouring agent. This study involves the refining agents arsenic, antimony and cerium combined with the colouring agents copper, manganese, chromium and iron.

Experimental

A soda-lime base glass given in Table 2 was used. In the experimental setup 5 g sodium nitrate per 100 g of sand was added as oxidising agent. Three different refining agents, antimony oxide, arsenic oxide and cerium oxide were compared to a glass without refining agent. Four different colouring ions were investigated. The used concentrations of colouring agents are:
0,2-2,0 mol% copper oxide,
0,4-2,0 mol% manganese oxide,
0,05-0,6 mol% chromium oxide and
0,3-1,2 mol% iron oxide. When pig-

Table 1 *The colour and the absorption peaks in nm of the most common ions of copper, manganese, iron and chromium in glass. The intensities of the absorption peaks are given as s = strong, m = medium and w = weak [2, 3].*

Wavelength	Colour	Ion	Ion	Wavelength	Colour
-	No colour	Cu^+ $\leftrightarrow$	Cu^{2+}	780 s, 450 w [2]	Blue
-	No colour	Mn^{2+} $\leftrightarrow$	Mn^{3+}	490 s [2]	Purple
1050 s [3]	Blue green	Fe^{2+} $\leftrightarrow$	Fe^{3+}	380 w, 420 w, 435 w [3]	Yellow green
365 s [2]	Yellow	Cr^{6+} $\leftrightarrow$	Cr^{3+}	450 w, 630 m, 650 m, 675 m [2]	Green

Table 2 *The composition of the used base glass in mol%. As_2O_3 or Sb_2O_3 are better refining agents than CeO_2, thus a higher amount of CeO_2 was used.*

Oxide	No refining agent	As_2O_3 / Sb_2O_3	CeO_2
SiO_2	72,21	72,00	71,64
Na_2O	9,96	9,96	9,96
K_2O	5,90	5,90	5,90
Al_2O_3	0,03	0,03	0,03
CaO	11,01	11,01	11,01
B_2O_3	0,89	0,89	0,89
Refining agent	0	0,21	0,59

ments were added the corresponding amount of sand was removed always keeping the alkaline level the same. The amount of arsenic oxide or antimony oxide was decreased to 0,1 mol% when manganese was used as colouring agent.

A glass batch corresponding to 146 g of glass was added in two charges into a ceramic crucible and melted at 1420 °C. The batch was stirred once and then left for 1½ hour before moulded into a cube 43x50x15 mm. When no refining agent was used the melt was left in the furnace for 18 h which gave a glass almost free from bubbles.

The colours were investigated by UV-VIS spectroscopy in the range 300-900 nm by use of a LKB Biochrom ultraspec II instrument. The examined glass pieces had parallel sides and were polished with Cerox prior to the measurement. The absorption spectra of the glasses containing refining agents but no colouring agents are given in figure 1. It is seen how the absorption of the glass with cerium oxide extends a little bit into the visible region. As a measure of the precision of the measurements, samples of the same glass piece and different melts with the same composition were measured. Eight such measurements containing 0,5 mol% copper oxide refined with arsenic oxide gave an absorption for 1 mm of 0,289 with a standard deviation of 0,02. The same amount of copper refined with antimony gave an absorption for 1 mm thickness of 0,101 with a standard deviation of 0,002.
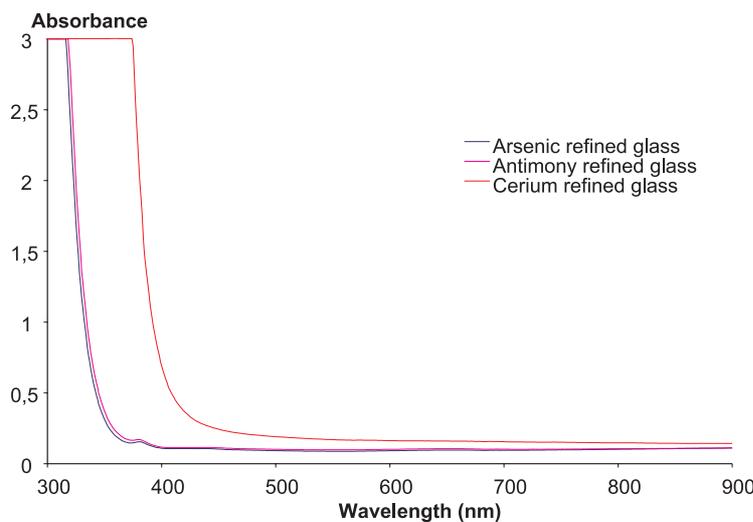
Figure 1 *The absorption of glasses containing refining agent but no colouring agent. The results are not corrected for the length of the glass piece but the antimony and the arsenic are very similar and the cerium refined glass sample is slightly shorter.*

Determination of the extinction coefficient for copper

There will always be a background absorption, A_0, not depending on the colouring agent but due to small imperfections of the surface or inhomogeneities in the glass matrix. The absorption of the glass, A, is then according to Lambert Beers law

$$A = A_0 + cl\varepsilon \qquad (1)$$

where c is the concentration of the colouring ion, l is the thickness of the glass sample in the light beam and ε is the extinction coefficient of the colouring ion. Cable et al have described a technique where the extinction coefficient of copper is approximated spectrofotometrically [4]. The method is based on the assumption that the equilibrium between copper(I) and copper(II) does not depend on the total concentration of copper. The absorption then becomes [4]:

$$A = A_0 + \varepsilon_{(Cu^{II})} [Cu^{II}] \qquad (2)$$

When just the total amount of copper is known equation 2 can be written as

$$\qquad\qquad\qquad\qquad (3)$$
$$A = A_0 + \frac{\varepsilon_{(Cu^{II})}}{1 + [Cu^I] / [Cu^{II}]} [Cu]$$

The slop of the line, b_T, for a specific melting temperature, T, is achieved by plotting A as a function of the copper concentration according to

$$b_T = \frac{\varepsilon_{(Cu^{II})}}{1 + [Cu^I]_T / [Cu^{II}]_T} \qquad (4)$$

Often it is possible to express the equilibrium constant, K', as a function of the concentration and not the activities.

$$K' = \frac{[Cu^{II}] [O^{2-}]^{1/2}}{[Cu^I] p(O_2)^{1/4}} \qquad (5)$$

Glass melts usually show predictable variations with temperature and the equilibrium constant can be expressed as a function of the enthalpy. If the oxygen concentration and the partial pressure of the oxygen are included in the constant the following expression is achieved

$$\log\left[\frac{[Cu^I]}{[Cu^{II}]}\right]_T = \frac{\Delta H}{2,303RT}\text{ -Z'} \qquad (6)$$

The experiments are performed at three different temperatures, 1-3, fulfilling equation 7.

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{T_2} - \frac{1}{T_3} \qquad (7)$$

By inserting equation 4 and 6 into equation 7 the extinction coefficient for copper(II) will be:

$$\varepsilon_{(Cu^{II})} = \frac{b_2^2\,(b_1 + b_3)\text{- }2b_1b_2b_3}{b_2^2\text{- }b_1b_3} \qquad (8)$$

The extinction coefficient for copper(II) can be determined from absorption measurement of copper containing glasses produced at three different temperatures. The absorption variation with concentration and temperature can be seen in figure 2. When the three slopes b_1 to b_3, given in table 3, are inserted into equation 8 the extinction coefficient becomes 16,6 dm^3/cm/mol.

Results and discussion
The composition of the glass Cable used to determine the extinction coefficient for copper(II) was 70,4 mol% SiO$_2$, 17,6 mol% Na$_2$O and 12,0 mol% CaO and their extinction coefficient is 21,7 dm^3/cm/mol compared to 16,6 dm^3/cm/mol that is determined for the base glass used in this study [4]. Cable has showed that both the basicity of the glass and which kind of ions that is found in the secondary coordination sphe-
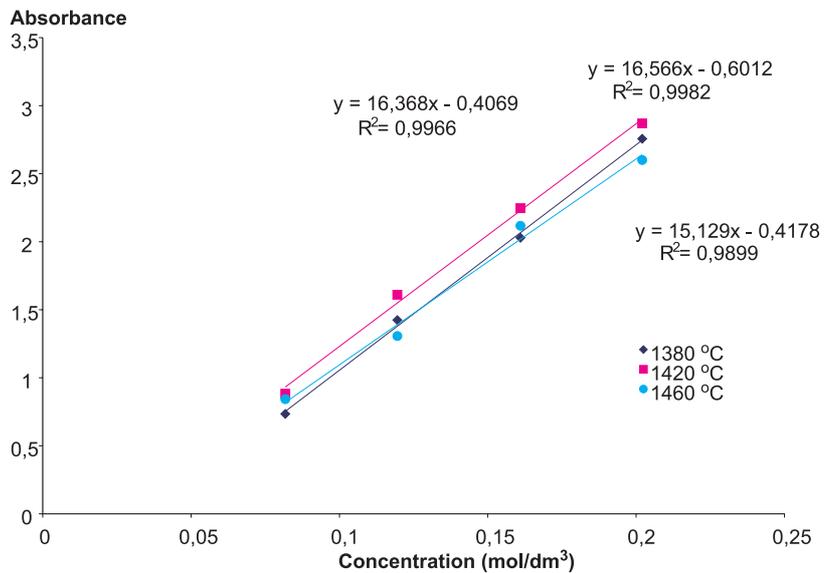
Figure 2 The absorption per cm at 780 nm as a function of the copper concentration for glasses melted at three different temperatures.

re will influence the extinction coefficient of copper(II) [1]. The total amount alkali metals is higher in the glass made by Cable than in our glass and thus the basicity should differ. We also have potassium ions in our glass and both these factors will influence the extinction coefficients of copper(II). The extinction coefficient increases with glass basicity [1] and the basicity, determined according to Duffy et al, of Cable's glass is 0,586. Our glass has a lower basicity of 0,579 which leads to the expectation of a lower value of the extinction coefficient of copper(II) in our base glass [5]. There are indications that the difference in extinction coefficient between these glasses might be too large. Cable has published an empirical equation to calculate the extinction coefficient of copper(II) according to

$$\varepsilon_{(Cu^{II})} = 27,63\text{ - }107,3\,[N]+ 264,8\,[N]^2 + 24,86\,[C] \qquad (9\,[6])$$

where N is the molar ration between sodium and silica and C is the molar ratio between calcium and silica. If this is applied to the base glass used and the potassium is counted as sodium, which will neglect the

fact that the different ions do influence the extinction coefficient, the extinction coefficient turns out to be 20,7 dm^3/cm/mol. The calculation compared to the spectrofotometrical determination would indicate that the ions of the secondary coordination sphere would influence the value more than the total amount of the alkali metals and that is not likely. These differences in extinction coefficient will greatly influence the calibrated ratio between copper(I) and copper(II). These results will therefor be compared to results from chemical analyses of the total amount of copper and the amount of copper(I) in the glass, before the extinction coefficient can be fully determined.

Table 3 *Comparison between Cable's [4] results and the results of this investigation. The absorption is given for a wavelength of 780 nm.*

[Cu] mol/dm³	Abs 1353°C [4]	Abs 1400°C [4]	Abs 1450°C [4]
0,0849	1,1976		1,734
0,149	3,205	2,687	2,605
0,212	4,172	3,939	3,534
A_0	0,4823	0,3462	0,3831
B	17,63	16,46	15,08
This study	1378°C	1417°C	1457°C
0,0819	0,7346	0,8829	0,8426
0,1197	1,424	1,611	1,306
0,1606	2,039	2,247	2,118
0,2013	2,756	2,869, 2,97	2,600
A_0	-0,6167	-0,4223	-0,4312
B	16,566	16,368	15,129
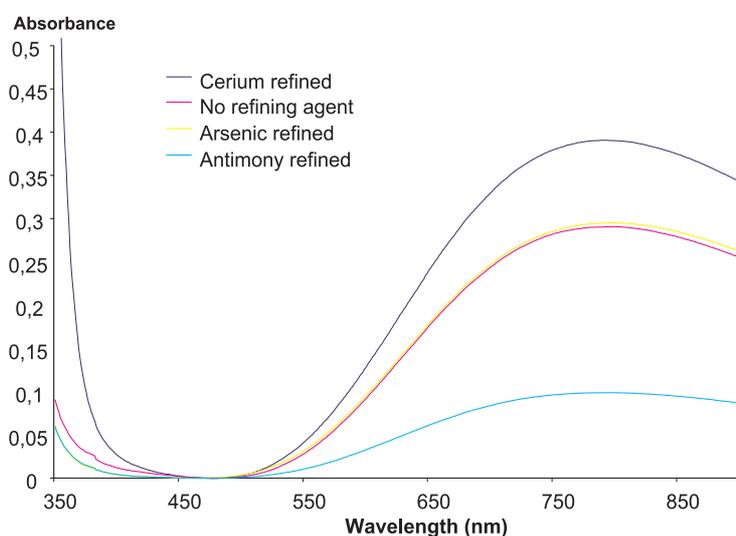
Figure 3 *The absorption of glasses coloured with 0,5 mol% copper and refined with antimony, arsenic, cerium and no refining agent. The spectra are background corrected and scaled to the same thickness.*

In figure 3 the absorption as a function of the wavelength is given for copper coloured glasses refined with different refining agents. The absorption of the antimony oxide refined glass is much lower than found for the other glasses and the colour of the glass is markedly weaker than colour of the glasses containing other refining agents. Arsenic oxide and no refining agents give similar results. The differences are within the standard deviation achieved for copper coloured glass refined with arsenic oxide. However, cerium oxide refining gives the strongest colouring effect in the glass. The fact that cerium actually oxidises copper in a soda-lime-silica glass has also been observed by Cable [1]. The refining agent does not change the absorption maximum for copper(II). The antimony refined glass gives a very flat absorption curve with 0,5 mol% copper but the position of the peak was confirmed by a sample with four times as much copper. This indicates that the dif-

ferent refining agents do not change the coordination geometry of the copper ion. The reducing order for the investigated refining agents is in agreement with the results of Cable [1].

Manganese colouring is very sensitive whether arsenic oxide or antimony oxide refining are used. Although the amount of antimony was decreased to half the amount, the glass just had a weak brownish colour, see figure 4. The absorption and the colour increases with arsenic and cerium but the highest absorption is observed when no refining agent at all is used. Paul describes different factors that influence the oxidation-reduction equilibrium in an oxide melt [7]. Important factors are oxygen pressure, the equilibrium constant and the activity of the oxides. In a melt with arsenic oxide and manganese oxide, there is quite a strong colour. Upon cooling, no oxygen from the atmosphere will enter or leave the system and a certain oxygen pressure is achieved within the glass. The arsenic oxides give rise to a lower oxygen pressure than the manganese oxide and thus will arsenic reduce manganese on cooling. This will proceed until the increased viscosity prevents any oxidation-reduction reactions [7]. Paul has also studied cerium oxide and found that it will reduce manganese less than arsenic oxide, in good agreement with our results. We found that antimony reduces manganese even more than arsenic so hardly any manganese(III) remains after cooling.

Cerium oxide is thus the refining agent giving the strongest coloration. It is known that cerium oxide influences the solarisation properties, but the effect is very much depending on the composition of the glass. In sodium silicate glass cerium is reported to prevent solarisation but in glasses with other polyvalent components, cases are found
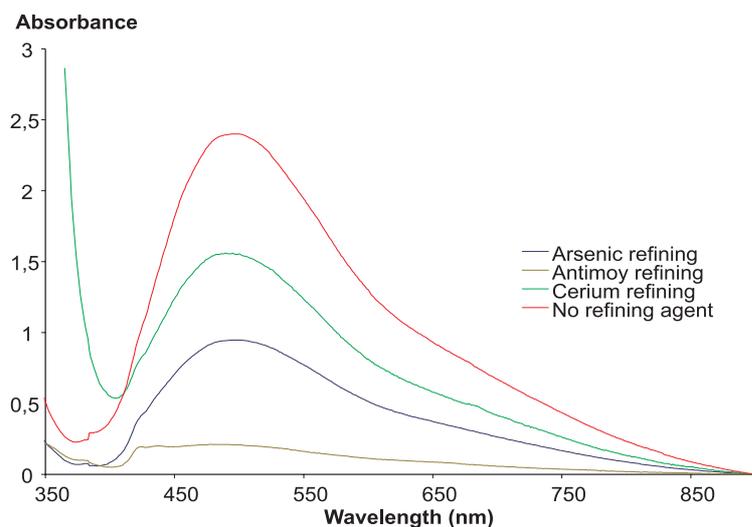
Figure 4 *The absorption of glasses coloured with 1,0 mol% manganese and refined with antimony, arsenic, cerium and no refining agent. The spectra are background corrected and scaled to the same thickness.*
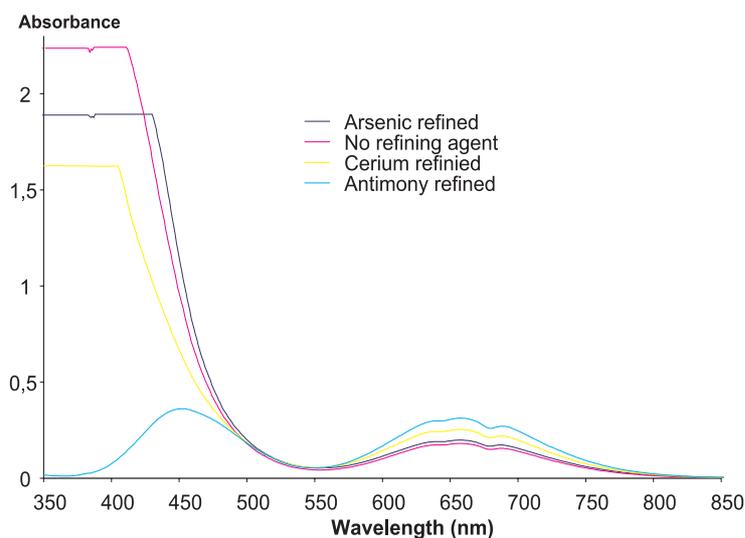
Figure 5 *The absorption of glasses coloured with 0,2 mol% chromium and refined with antimony, arsenic, cerium and no refining agent. The spectra are background corrected and scaled to the same thickness.*

where cerium oxide increases the solarisation effect [8]. The influence of cerium on the solarisation of the manganese coloured glass was tested by illuminating a sample with a high power UV-lamp for two weeks. Absorption measurements before and after radiation did hardly show any change of the absorption curve.

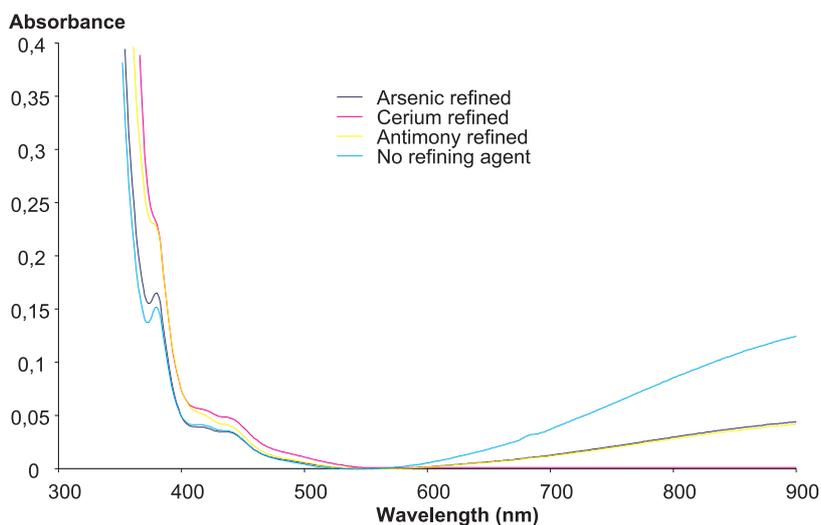Chromium(VI) has a very strong extinction coefficient with an ab-

sorption maximum at around 365 nm. Lee et al determined the extinction coefficients for chromium (VI) and chromium(III) in a glass with the composition 73 weight% SiO_2, 16 weight% Na_2O and 11 weigth% CaO to 4246 and 21,5 dm^3/cm/mol, respectively [9]. With our instrumentation it is not possible to resolve the chromium(VI) peak. This peak covers completely the ab-

sorption band at 450 nm due to chromium(III). The only sample without chromium(VI) is the antimony refined glass in which the band at 450 nm is very clear, see figure 5. This result agrees well with the results of Leister that all chromium is reduced to the chromium(III) state when antimony is added [10]. A yellow tint is introduced to the cerium oxide refined glass, in which we have some chromium(VI). The yellow colour increases when refining is done with arsenic oxide and is strongest in the sample without refining agent due to an increasing amount of chromium(VI).

Iron(III) has three absorption bands at 380, 420 and 435 nm while iron(II) absorbs at 1050 nm [3]. In figure 6 the absorption for the four different refined glasses with 0,5 mol% iron is shown. No refining agent results in the highest amount iron(II) and thus a more blue-green colour. Refining with antimony or arsenic oxide gives similar results, the concentration of iron(III) increases and a more yellowish colour of the glass is observed. Cerium oxide refining oxidises all the iron to iron(III). The broad band at 1050 nm due to iron(II) disappears completely, see figure 6. The molecular extinction coefficient for iron in a glass with the composition 73 % SiO_2, 13% Na_2O and 9% CaO most likely given in weight percent is reported to be 4,1 for the iron(III) peak at 380 nm and 31,7 for the iron (II) peak at 1050 nm [11]. Thus it is likely that the sensibility for iron(II) is somewhat higher than for iron(III) although we are measuring at the wavelength 900 nm.

Conclusions

The most reducing refining agent for copper, chromium and manganese is antimony oxide while the most reducing conditions in the iron coloured glass occur without addition of refining agent, see table 4.

Absorbance (y-axis)

Legend:
- Arsenic refined
- Cerium refined
- Antimony refined
- No refining agent

Wavelength (nm) (x-axis)

Figure 6 The absorption of glasses coloured with 0,5 mol% iron and refined with antimony, arsenic, cerium and no refining agent. The spectra are background corrected and scaled to the same thickness.

Cerium oxide refining gives the most oxidising conditions for copper and iron while a melt without added refining agent gives the most oxidising conditions for manganese. For chromium no refining agent or arsenic oxide refining give corresponding results.

In most glasses there is a measurable amount of the coexisting ions of each colouring metal but antimony oxide refining reduces chromium so efficiently that there are only negligible amounts of chromium(VI) in the sample. Cerium oxide refining on the other hand, oxidises iron so there are no detectable amounts of iron(II).

The series of reducing power indicated in this study is thus for copper coloured glass, Sb>As>Cu>Ce, for chromium coloured glass, Sb>Ce>As,Cr, for manganese coloured glass, Sb>As>Ce>Mn, and for iron coloured glass, Fe>As,Sb>Ce.

This study is to be continued and the extinction coefficients for the colouring agents will be determined.

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Table 4 The influence of the refining agent on one of the two existing metal ions of each colouring agent; the numbers are the absorbances at the absorption peak and are given for 1 mm thickness. The most reducing refining agent is given first in the table.

Copper(II)		Chromium(III)		Manganese(III)		Iron(II)	
Sb	0,101	Sb	0,312	Sb	0,021	Nothing	0,121
As	0,289	Ce	0,253	As	0,094	As	0,043
Nothing	0,290	Nothing	0,179	Ce	0,156	Sb	0,041
Ce	0,400	As	0,180	Nothing	0,240	Ce	-0,003

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