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Fast and accurate analysis of silver and halides in glasses by stepwise potentiometric titration

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An analysis of silver and halides in glasses is reported. The method requires only one decomposition of the glass, followed by the conversion of the silver chloride and/or bromide precipitates into silver iodide by a known addition of excess potassium iodide and subsequent stepwise potentiometric titration of the halides with silver sulphate. The time required for the complete analysis of the ground glass is 2 h. Presence of silver and iodide in the glass necessitates an additional, independent, determination of one of these elements. Experimental conditions are given and discussed, the reproducibility of the method is reported.

Analyse rapide et précise de l'argent et des halogénures dans les verres par titrage potentiométrique par parliers

On traite d'une méthode d'analyse de l'argent et des halogénures dans les verres. Cette méthode nécessite une attaque du verre, qui est suivie d'une transformation des précipités de chlorure et/ou bromure d'argent en iodure d'argent par d'un excès connu d'iodure de potassium et d'un titrage potentiométrique par paliers des ions halogénure avec du sulfate d'argent. Deux heures sont nécessaires pour une analyse complète du verre broyé. La présence d'argent et d'iodure dans le verre nécessite la détermination supplémentaire d'une de ces éléments séparément. Les conditions expérimentales sont présentées et discutées, la reproductibilité de la méthode est examinée.

Schnelle und genaue Analyse von Silber und Halogeniden in Gläsern durch stufenweise potentiometrische Titration

Eine Analyse von Silber und Halogeniden in Gläsern wird beschrieben. Bei dieser Methode wird lediglich ein Aufschluß des Glases benötigt, dem die Umwandlung der Silberchlorid- und/oder -bromidniederschläge in Silberjodid durch Zugabe eines bekannten Kaliumjodidüberschusses und eine stufenweise potentiometrische Titration der Halogenidionen mit Silbersulfat folgen. Für die vollständige Analyse des gemahlenen Glases sind zwei Stunden notwendig. Die Gegenwart von Silber und Jodid im Glas erfordert die zusätzliche, unabhängige Bestimmung eines dieser Elemente. Experimentelle Bedingungen werden angegeben und diskutiert, die Reproduzierbarkeit der Methode wird mitgeteilt.

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1. Introduction

Analytical methods usually applied for the quantitative determination of silver, chloride, bromide, and, rarely, iodide in photochromic glasses have certain draw-backs in that they either depend on glass composition and require calibration standards (x-ray fluorescence [1], neutron activation), or do not distinguish between the different halides (controlled-potential coulometry [1], spectrophotometry of halide complexes [2]), or are rather time-consuming (wet-analytical methods employing gravimetry [3], titrimetry [1], and atomic absorption spectrocopy and requiring several different glass decompositions). In this paper a brief report is given on an accurate and time-saving, absolute titrimetric method, developed and applied in this laboratory [4], which consists of one glass decomposition step, conversion of the silver bromide and chloride precipitates formed into less soluble silver iodide by a known quantity of added excess potassium iodide, and potentiometric titration of the halides with silver sulphate solution. The time required for the complete analysis of silver, chloride, and bromide is three hours, including one hour of grinding. Presence of iodide and silver in the glass necessitates an additional, independent determination of one of these elements. The method is applicable to glasses containing any single, or any combination, of the elements.

2. Experimental procedure

The entire analysis, including glass decomposition, is carried out under argon at 0 to 5 °C within a jacketed, closed, PTFE cell with standard tapers. Pt lining of the internal surface of the cell excludes adsorption and depositions which would be difficult to remove from PTFE.

After grinding to a particle size below 10 μm, an appropriate amount of usually 0,1 to 1 g of the glass is decomposed under stirring (magnetic stirrer) by a mixture of 16,4 g fluoric acid (40 %), 9,4 g sulphuric acid (96 %) (both E. Merck, Darmstadt; Suprapur® quality) and 5 g water. The decomposition is completed within 30 to 35 min. A known volume of 10^{-2} molar KI and, if advantageous or necessary (see section 3.), of 10^{-2} molar KBr and/or KCl solutions are then slowly added, and the solution is diluted to 50 ml without allowing the temperature to rise above 5 °C. The cell content is stirred for 45 to 50 min, during which AgCl and/or AgBr are converted into AgI. After introducing a silver electrode (Schott Geräte Hofheim, type Ag 110) and a double junction reference electrode (Schott Geräte Hofheim, type äB 222) and the specially designed PTFE tip of an automatic titrator (Schott Geräte Hofheim, type TS 165, T 100, TA 20), the halides are titrated with 0,01 N Ag_2SO_4 solution at a rate of 0,4 ml/min during 20 to 30 min. From the steps of the recorded emf vs. volume plot the contents of the halides in the solution are calculated taking into account the amounts of bromide and/or chloride added before the titration. The silver content is obtained from the difference of added and titrated iodide.

3. Reproducibility and accuracy

Reproducibility and accuracy of the results are mainly given by the evaluation of the emf/volume plots obtained. The approximate accuracy was determined by analysing a number of different glasses spiked with differing amounts of silver, chloride, and bromide. Results for silver were also compared with those obtained by atomic absorption spectroscopy.

Most accurate results are obtained when only one of the elements is present. In this case, both, reproducibility and accuracy can be represented by (0,05 to 1,5) ± 0,002 wt % for Ag_2O, Br, and Cl corresponding to (±4 to ± 0,13) % of the element present. For more than one element, optimum results are obtained if comparable equivalent amounts are titrated. It is thus advantageous to add known amounts of KCl and/or KBr to the solution in order to achieve this condition. The reproducibility can then be given as (0,05 to 1,5) ± 0,005 wt % for Ag_2O, Br, and Cl. For glasses with the usual content of 0,1 to 0,3 wt %, this corresponds to (±5 to ± 1,7) % of the elements present. The accuracy is approximately comparable to this figure. The exact number will be confirmed by comparison with other, well established, though time-consuming, methods.

4. Special notes

The method yields accurate results only if the reported experimental conditions are strictly observed. The following points concerning the fundamentals of the method are particularly noted:

a) Loss of hydrogen halides by evaporation from the relatively concentrated acid solution is avoided by keeping the temperature below 5 °C. Halide solutions and water must thus be added slowly and carefully while the cell content is vigorously stirred.

b) Hydrogen iodide is sensitive to oxidation. The entire analysis, including addition of solutions and introduction of electrodes through the tapers of the cell, must thus be carried out under argon. Since even low concentrations of nitrate were found to oxidize iodide under the prevailing conditions, silver sulphate solution (instead of silver nitrate) is used for the titration, and potassium sulphate (instead of potassium nitrate) serves as the bridging electrolyte of the double junction reference electrode.

c) The conversion of the silver halides is completed in reasonable periods only as long as AgBr and AgCl precipitated during the glass decomposition consist of fine crystals. The decomposition step should thus last not longer than 35 min and should immediately be followed by the conversion of the silver halides.

d) Coprecipitation of different silver halides during stepwise argentometric titration is suppressed by several electrolytes, e.g. $Al(NO_3)_3$ [5], $Ce(NO_3)_3$ [5], $Ba(NO_3)_2$ [6], and KNO_3 [5 and 6]. According to the experiments, this effect is also achieved by high hydrogen ion concentrations. An optimum was found for the concentrations of the finally diluted acid at sufficiently low titration rates. The reported acid concentrations and titration rate should thus strictly be observed. Application of an iodide-sensitive membrane electrode is not recommended because of longer response times and thus more sluggish emf volume plots. The low temperature applied during the titration has the additional advantage of increasing the height of the emf steps due to the temperature-dependent solubility products of the silver halides [7] and thus increases the sensitivity and accuracy of the method.

5. Interferences

Due to the presence of hydrogen iodide the method is basically sensitive to oxidizing compounds, and most polyvalent ions in the higher oxidation state, if they were present, would have to be reduced by an appropriate reducing material. Ascorbic acid has been applied successfully [8] but has less reducing power in the acidic decomposing solution because of the pH dependence of the redox potential [9]. In practice the problem is substantially reduced as photochromic glasses rarely contain polyvalent ions. Even redox fining agents are almost never present, and Cu^{2+} ions often found in these glasses do not disturb the analysis.

Further glass ingredients tested for possible interferences were lead and barium, which are deposited as sulphates during glass decomposition but were not found to adsorb measurable quantities of the elements of interest. The same holds for ZrO_2 and TiO_2. Also, glasses containing phosphate or borate could be decomposed during the required time.

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