

A SIMPLE, DIRECT IC METHOD FOR THE DETERMINATION OF SILICATE IN SUGAR PROCESSING STREAMS

SN WALFORD

Sugar Milling Research Institute, University of Natal, Durban, 4041, South Africa

Abstract

An ion chromatographic method for analysing silicates in sugarcane juices has been developed. It has advantages of speed, potential automation and lack of interference from other constituents in juice.

Keywords: silicate, ion chromatography

Introduction

Sugarcane absorbs more silicon than any other mineral nutrient and can store it in the form of insoluble silicagel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and soluble silica (silicic acid H_3SiO_4^-) (Samuels, 1969; Meyer and Keeping, 2000). Evidence suggests that silicon prevents aluminium and manganese toxicity and helps protect the plant from pest and fungal disease. In the expressed juice, silicon compounds have been shown to be important in the control of sucrose inversion in both the rawhouse and refinery (Alexander *et al.*, 1971; Alexander, 1957). Silica can precipitate in the later effects of the evaporator train and pans leading to process inefficiencies (Walthew and Turner, 1995).

Analysis of the soluble inorganic form is based on the reaction between silica and ammonium molybdate and measurement of the resultant yellow colour of the reduced form of the complex (Davies *et al.*, 1938; Alexander and Parish, 1953). Reducing substances used include hydrosulphite, a metabisulphite sulphite/1-amino-2-naphthol-4-sulphonic acid mixture and tin-II-chloride. Care has to be taken to maintain the pH between 5.8 and 6.2 when developing the colour to prevent reduction of phosphomolybdate and subsequent interference. Molybdosilicic acid can exist in two forms (α - and β -molybdosilicic acid) each of which has a different absorption maximum (Strickland, 1952; Truesdale and Smith, 1975). Factors affecting complex formation include reactant concentration and composition, pH, analysis time, ionic strength of the sample solution and presence of other compounds such as acetic acid. Sugarcane juices are buffered which can lead to inconsistencies with final solution pH when compared to the standards.

Ion chromatography (IC) offers an alternative, direct method of silicate analysis. This poster describes the IC method using a Hamilton PRP-X100 column and conductivity detection. Method development, linearity, recovery and possible interference from other juice constituents are discussed.

Experimental

Apparatus

A Metrohm 761 ion chromatograph consisting of pump, injector and conductivity detector controlled by Metrohm IC-Net 1.1

software was used for the analyses. A Linear PHD 201 variable UV detector was used at a wavelength of 210 nm with the output connected to a HP3396 integrator connected to a HP Peak data collection system for the simultaneous detection of UV absorbing compounds. Separation of ions of interest was achieved using a Hamilton PRP-X100 anion exchange column (4.6 x 150 mm, 7.5 μm particle size, 0.17 mequiv/g ion exchange capacity) at room temperature.

Reagents

The eluent (3.2 mmol/L sodium hydroxide / 0.5 mmol/L sodium carbonate) was prepared daily with freshly distilled water and used at a flow rate of 1.3 ml/min. A stock silicate standard solution (1000 ppm SiO_2) was prepared by dissolving 100 mg pure SiO_2 in 0.2% sodium hydroxide solution (with warming) and making to 100 ml. All silicate solutions were stored in polyethylene bottles to minimise contamination. Appropriate dilutions were made to give the required standards.

Sample preparation

Samples are diluted with silica-free water (DAC 1:10; MJ, CJ and syrup 1:25), filtered (0.45 μm) and injected (100 μl).

Results and Discussion

Hydroxide eluent for the IC determination of silica was first described by Okada and Kuwamoto (1985). Sodium hydroxide solution is a weak chromatographic eluent (Haddad and Jackson, 1990) resulting in long retention times for ions such as chloride and sulphate. A further drawback is the lack of buffering capacity (especially when analysing factory solutions). However hydroxide is ideal for the weakly ionised silicic acid ($\text{p}K_1 = 9.8$; $\text{p}K_2 = 12.16$). The addition of sodium carbonate overcomes the buffering problem and reduces the retention time of other ions (Metrohm, 2001).

Sugars are routinely analysed at the SMRI on anion exchange resins using eluents at high pH (Schäffler, *et al.*, 1996) at orders of magnitude higher in concentration. No interference with the silicate peak was found for glucose, fructose and sucrose at concentrations found in typical samples.

Factory process solutions contain mixtures of organic acids including acetic, formic, lactic, glycolic and aconitic acids. Analysis of solutions of these acids showed no interference with the silicate peak. This was confirmed by simultaneous analysis of the acids by UV detection at 210 nm. Fluoride interference is possible under these conditions but significant levels of this ion should not be present in sugar solutions. The concentration of the carbonate in the eluent can be modified to resolve

these peaks at the expense of buffering capacity and retention time.

The IC method described is shown to be linear over a wide range (0.5 to 50 ppm SiO₂) and useful for factory process solutions including DAC, MJ, CJ, syrup and sugars. The peaks eluting between silica and organic acids/carbonate peak have UV absorbances and conductances. They are believed to be due to ionised colour compounds as evidenced by their disappearance when removed from the solution by C18 SPE treatment.

Conclusions

A simple, direct IC method for the analysis of silicate in sugar factory streams has been developed that takes ten minutes per sample. Automation of the analysis is possible for large sample studies. The method has been found to be linear and free of interference from typical factory constituents and could be useful in clarification and evaporation studies.

References

Alexander, AG, Acin-Diaz, N and Montalvo-Zapata, R (1971). Inversion control in sugarcane juice by sodium meta-silicate. *Proc Int Soc Sug Cane Technol* 14:794-804.

Alexander, JB (1957). Some observations on the filterability of Natal raw sugars. *Proc S Afr Sug Technol Ass* 31:68-75.

Alexander, JB and Parish, JR (1953). Silica in raw and clarified cane juices. *S Afr Sug J* 573-579,589.

Davies, JG, Gomez, AC and Boon, D (1938). The estimation of soluble silica in cane juice. *Int Sug J* 40:105-106.

Haddad, PR and Jackson, PE (1990). Eluents for ion-exchange separations. *Ion Chromatography. Principles and Applications*. Elsevier, Amsterdam. p89.

Metrohm (2001). Silicate in drinking water. IC Application Work AW CH6-0695-052001.

Meyer, JH and Keeping, MG (2000). Review of research into the role of silicon for sugarcane production. *Proc S Afr Sug Technol Ass* 74:29-40.

Okada, T and Kuwamoto, T (1985). Ion chromatographic determination of silicic acid in natural water. *Anal Chem* 57:258-262.

Samuels, G (1969). Silicon and sugar. *Sugar y Azucar* 64 (4) :25-29.

Strickland, JDH (1952). The preparation and properties of silicomolybdic acid. I-III *J Am Chem Soc* 74:862-876.

Schäffler, KJ, Morel du Boil, PG and Walford, SN (1996). HPAEC: Some precautions required for the reliable analysis of carbohydrates. *Proc S Afr Sug Technol Ass* 70:241-250.

Truesdale, VW and Smith, CJ (1975). The formation of molybdosilicic acids from mixed solutions of molybdate and silicate. *Analyst* 100:203-212.

Walthew, DC and Turner, LM (1995). Analysis of scale from some South African sugar mills. *Proc S Afr Sug Technol Ass* 69:138-143.

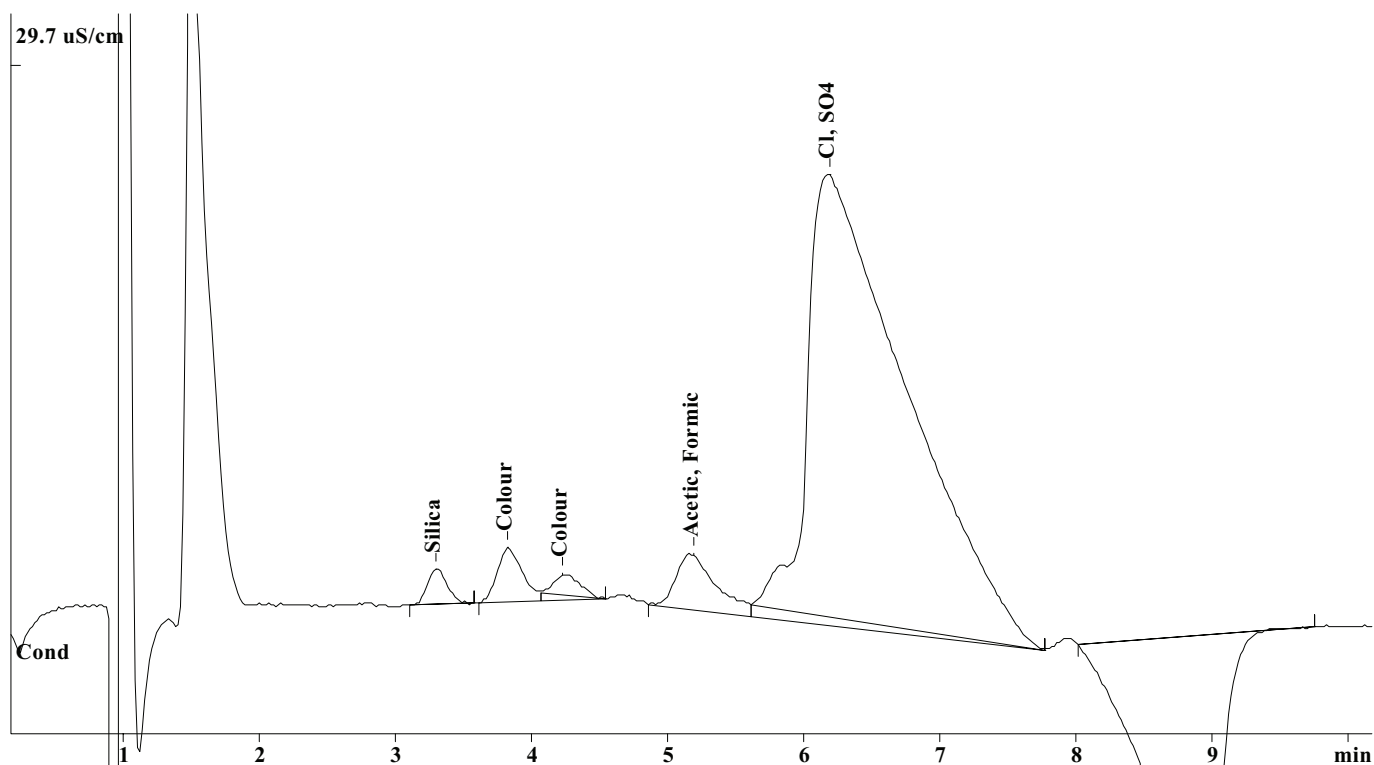


Figure 1. Chromatogram of MJ showing separation of silica from other components (sugars elute at 1.5 minutes).