

Short Communication

Sulphur compounds

CLIX[☆]. Determination of dithionite ($S_2O_4^{2-}$) and hydroxymethanesulphinic acid ($HOCH_2SO_2^-$; Rongalite) by ion-pair chromatography

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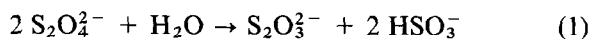
ABSTRACT

Dithionite ($S_2O_4^{2-}$) and hydroxymethanesulphinic acid ($HOCH_2SO_2^-$) were separated from other sulphur oxyanions by ion-pair chromatography and determined using a UV absorbance detector. To circumvent the autoxidation of dithionite it was derivatized by quantitative reaction with formaldehyde to give hydroxymethanesulphinic acid, the UV spectrum of the latter is reported. The detection limit of $HOCH_2SO_2Na \cdot 2H_2O$ (Rongalite) was 0.5 mg l^{-1} (0.5 ppm).

INTRODUCTION

Sodium dithionite and sodium hydroxymethanesulphinic acid (Rongalite) are commercial chemicals widely used as powerful reducing agents, in particular in the textile, printing and paper industries [2]. The determination of dithionite is difficult owing to its extreme sensitivity to oxygen in aqueous solution and to the spontaneous decomposition of such solutions even with exclusion of oxygen [3,4]. This decomposition depends strongly on the pH and is rap-

id at $\text{pH} < 5.5$. At pH values close to 7 the main decomposition reaction can be represented by the equation [5]



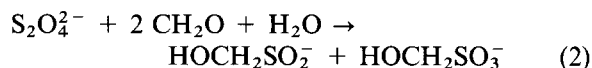
So far, dithionite has been determined by iodimetric [6,7], potentiometric [8], and spectrophotometric [8] titration, polarography [9], Raman spectroscopy [10] and spectrophotometry [11]. Reports on the ion chromatographic determination of dithionite [12] will be discussed below.

Inorganic sulphide (HS^-), polysulphide (S_n^{2-}), sulphite (SO_3^{2-}), thiosulphate ($S_2O_3^{2-}$), polythionates ($S_nO_6^{2-}$) and organic S-sulphonate anions ($RSSO_3^-$) can be separated and determined by ion-pair chromatography [13–15]. This method uses an

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inert organic stationary phase and a water–acetonitrile mixture containing tetrabutylammonium ions and a buffer as the mobile phase. A UV absorbance detector has been applied in all instances. We report here the analysis of aqueous dithionite and Rongalite by ion-pair chromatography. To circumvent the oxygen sensitivity of dithionite, the freshly prepared solutions were reacted with formaldehyde, which converts $S_2O_4^{2-}$ rapidly and quantitatively into the less sensitive sulphinate and sulphonate ions [6,7].



EXPERIMENTAL

The chromatographic and spectroscopic equipment described in a previous paper [14] were used. The variable-wavelength UV detector was operated at 215 nm. As in the earlier work [14], a PRLP-S column (Polymer Labs) (120 mm × 4 mm ID, particle size 8 μm) connected to a PRP-100 precolumn (Knauer) (Eurogel, particle size 8 μm) was used. Two different eluent compositions were employed, depending on the accompanying ions to be determined. For mixtures of $S_2O_4^{2-}$ with $S_2O_3^{2-}$ and polythionates the eluent was water–acetonitrile (Promochem Chrom AR) (75/25, v/v) containing 1 mmol l⁻¹ of Na₂CO₃ and 2 mmol l⁻¹ of tetra-*n*-butylammonium hydrogenphosphate (pH of eluent = 7.7). Mixtures of $S_2O_4^{2-}$ with HS⁻ and $S_2O_3^{2-}$ were analysed with an eluent consisting of water–acetonitrile (93/7, v/v) containing 1 mmol l⁻¹ of Na₂CO₃ and 2 mmol l⁻¹ of tetra-*n*-butylammonium hydroxide. The pH of this eluent was adjusted to 11.0 by addition of H₃PO₄ (8%). The eluents were degassed and in some instances oxygen-free helium was bubbled through. However, even then it was not possible to detect $S_2O_4^{2-}$ directly [16]. The flow-rate was always 1 ml min⁻¹.

Water for sample and eluent preparation was doubly distilled. To remove dissolved oxygen, the water for samples was then refluxed under nitrogen for 10 h. The nitrogen had an oxygen content of <0.1 ppm. To avoid the intrusion of O₂ from the air, the apparatus was made from glass and copper and the use of plastic pipes was avoided as far as possible.

Na₂S₂O₄ (93%, containing 6.5% Na₂SO₃ and 0.5% Na₂SO₄) (BASF) and Rongalite (98.8% dihydrate) (BASF) were used as received. Na₂S₂O₄ was stored at -18°C under nitrogen. Na₂S₂O₃ · 7H₂O (Merck) was recrystallized from degassed water. Aqueous formaldehyde (37%) (Merck), Na₂SO₃ (puriss.) (Fluka) and K₂S₂O₃ · 3/2H₂O (purum) (Fluka) were used as received. Polythionates were prepared in almost 100% purity according to ref. 17.

To calibrate the chromatographic system, standard solutions of Rongalite and dithionite were made daily. The latter was added directly to aqueous formaldehyde of pH 8–9. To study the decomposition of aqueous dithionite (see below), the $S_2O_4^{2-}$ solution (ca. 20 mmol l⁻¹, 1 ml) was added to aqueous formaldehyde (2 ml) which had been adjusted to pH 8–9 with NaOH (0.1 mol l⁻¹) followed by dilution to 50 ml with doubly distilled water. After completion of reaction 2, exclusion of oxygen was no longer necessary.

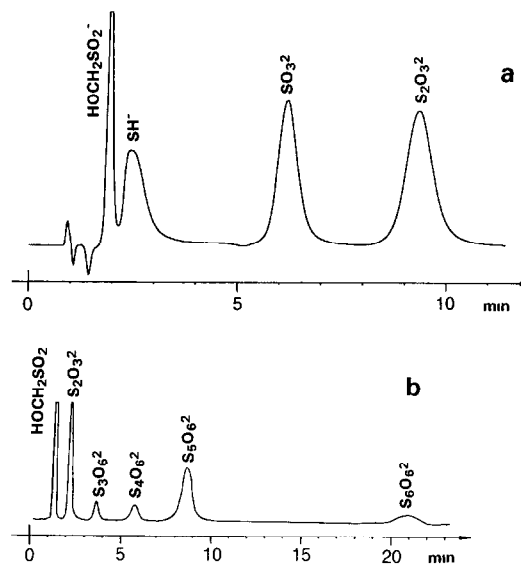


Fig. 1. Chromatograms of the following mixtures: (a) HOCH₂SO₂⁻ (0.75 mmol l⁻¹), HS⁻ (0.44 mmol l⁻¹), SO₃²⁻ (0.80 mmol l⁻¹) and S₂O₃²⁻ (0.70 mmol l⁻¹) using an alkaline eluent (pH 11.0), (b) HOCH₂SO₂⁻ (0.39 mmol l⁻¹), S₂O₃²⁻ (0.39 mmol l⁻¹), S₃O₆²⁻ (0.90 mmol l⁻¹), S₄O₆²⁻ (0.03 mmol l⁻¹), S₅O₆²⁻ (0.09 mmol l⁻¹), S₆O₆²⁻ (0.02 mmol l⁻¹) using an almost neutral eluent (pH 7.7).

RESULTS

Fig 1a shows the chromatographic separation of hydroxymethanesulphinic acid, hydrogensulphide, sulphite and thiosulphate at pH 11.0 of eluent No. 2. In Fig 1b the corresponding separation of hydroxymethanesulphinic acid, thiosulphate and the polythionates $S_nO_6^{2-}$ ($n = 3-6$) is shown (eluent No. 1 at pH 7.7). The different retention times on the two chromatograms are due to the different eluent compositions. The assignment of the peaks was made using pure substances and by comparison of retention times and UV absorbance spectra recorded on-line with a diode-array detector [14].

Fig 2 shows the previously unknown UV spectrum of the sulphinate, identical spectra were obtained from either Rongalite or $S_2O_4^{2-}-CH_2O$ mixtures. The sulphinate does not absorb at 215 nm and therefore does not show up in the chromatograms of $S_2O_4^{2-}-CH_2O$ mixtures. However, when the alkaline eluent was used it was observed that the sulphinate partly hydrolyzed to give sulphite and CH_2O during analysis. Whereas CH_2O does not absorb at 215 nm the sulphite peak was well separated (see Fig 1a). As neither sulphide, thiosulphate nor polythionates react with CH_2O at 20°C in water, all these species, which have been found in decomposing dithionite solutions, can now be determined by ion-pair chromatography. However, sulphite reacts with CH_2O to give the sulphinate which, as mentioned above, does not absorb at 215 nm. Its determination requires the use of another detection technique.

The calibration functions for Rongalite and di-

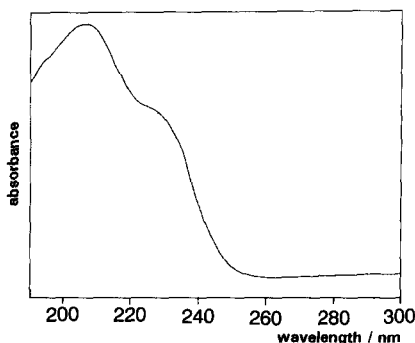
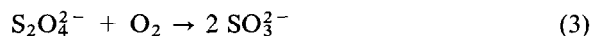


Fig 2 Absorption spectrum of the $HOCH_2SO_2^-$ ion in water-acetonitrile (75:25, v/v) at pH 7.7 recorded with a diode-array detector. No absorptions were detected in the range 300–800 nm.

tionite (after reaction with CH_2O) were investigated in the concentration range (c) 0.09–0.46 $mmol\ l^{-1}$. Straight lines were obtained in both instances (correlation coefficients $r \geq 0.999$), the slopes of which differed by only 1.6%. Rongalite, peak height = $974c - 12.2$, dithionite, peak height = $959c - 11.7$. The negative intercepts expected for $c = 0$ are caused by the negative peak preceding the sulphinate peak. In both instances the concentration of the solution was determined by iodimetric titration of the sulphinate. The results show that reaction 2 must proceed rapidly and quantitatively. Using a sample loop of 10 μl the detection limit of Rongalite ($HOCH_2SO_2Na \cdot 2H_2O$) was 0.5 $mg\ l^{-1}$.

To test the applicability of the method, we analysed an aqueous dithionite solution exposed to air simultaneously by iodimetric titration and by quantitative ion-pair chromatography. The results shown in Fig 3 demonstrate that both methods yield virtually identical values. Owing to the reaction



the dithionite concentration (c) slowly decreased but in between sometimes oscillations of c occurred, as had already been observed by others [18]. A more detailed account of the dithionite decomposition will be published elsewhere.

DISCUSSION

We have demonstrated that dithionite can be determined chromatographically after derivatization.

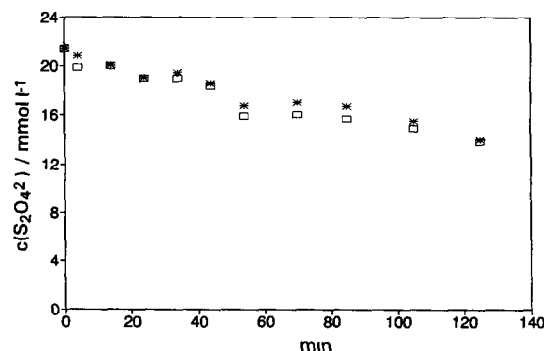


Fig 3 Autoxidation and decomposition of aqueous sodium dithionite on exposure to air (initial pH = 7). The $S_2O_4^{2-}$ concentration was independently determined by (*) ion-pair chromatography and (□) iodimetric titration.

to the more stable hydroxymethanesulphinic acid, which has absorption maxima at 206 and 225 nm and can therefore be detected using a UV absorbance detector. The dithionite anion also shows a strong UV absorption (maxima near 200 and 320 nm [19,20]), but its extreme sensitivity to oxygen in solution prevented its direct chromatographic separation and UV detection. However, Stutts [12] reported the detection of $S_2O_4^{2-}$ by ion chromatography using a UV detector operating at 254 nm, although $S_2O_4^{2-}$ shows an absorption minimum near 260 nm. He added sulphite to the eluent to prevent autoxidation of the dithionite. However, Dixon [20] has demonstrated that dithionite reacts much faster with molecular oxygen than sulphite. Therefore, the use of sulphite as an antioxidant may remove the oxygen dissolved in the eluent, but oxygen diffusing into the system during sample handling will first oxidize $S_2O_4^{2-}$ rather than SO_3^{2-} . We therefore consider that our technique of immediate derivatization of dithionite and its indirect detection as sulphinate is superior. Not only is the sample handling simpler, but also the detection limit of 0.5 mg l^{-1} (0.5 ppm) is much lower than the 10 ppm reported for Stutts's method [12].

The separation of $S_2O_4^{2-}$ from other sulphur oxyanions by ion-pair chromatography reported by Weiss and Gobl [21] is in error as the peak assigned to dithionite was in fact due to sulphate [22].

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