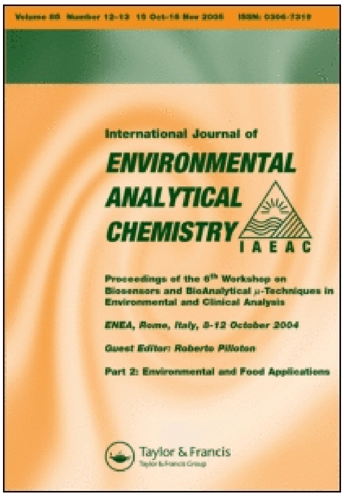

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New Chemiluminescence Methods for Environmental Analysis†

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Sulphide (≥ 0.1 ppb) is determined by the chemiluminescence generated by hydrogen peroxide oxidation in the presence of a catalyst (peroxidase, catalase or osmium tetroxide). Molecular emission cavity analysis is used to determine sulphate (> 100 ppb S) in waters by direct injection into the cavity, or > 10 ppb by reduction to hydrogen sulphide and transport of the gas to the cavity. Similar volatilization systems are described for arsenic, selenium, ammonia, silicon and fluorine.

KEY WORDS: Chemiluminescence, sulphide, sulphate, meca.

INTRODUCTION

Chemiluminescence is the emission of radiation from an excited atom or molecule produced by a chemical reaction:

$$A + B + \ldots \rightarrow P^*$$
$$P^* \rightarrow P + h\nu \text{ (chemiluminescence)}$$

It is also possible to transfer the excitation energy to another species (known as a sensitizer) which will emit radiation at a wavelength longer than that from the reaction product, and with a spectrum the same as that of the fluorescence emission spectrum of that species.

Chemiluminescence may be observed in liquids and in gases,[1] and has been widely used for measurement of atmospheric NO_x, SO_2, ethylene and ozone. In this paper, some newer applications of chemiluminescent

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reactions will be reviewed, one in solution, the others in hydrogen-based flames, which have particular relevance to environmental analysis.

DETERMINATION OF PPB LEVELS OF SULPHATE IN SOLUTION

Klockow and Teckentrup[2] have recently described the chemiluminescence generated by the hypohalite oxidation of sulphide in alkaline solution. Using methylene blue as sensitizer, as little as 10^{-7} M sulphide could be determined. An investigation of this and related reactions has greatly increased the sensitivity of the determination.[3] Replacement of the hypohalite by hydrogen peroxide, and addition of a suitable catalyst gives up to a hundred-fold increase in sensitivity. Osmium tetroxide or peroxidase is the most effective catalyst, both giving detection limits of 0.1 ppb (0.15 ng) of sulphide, and linear log-log calibration ranges up to 10 or 100 ppm, respectively. Catalase gives a detection limit of 1 ppb, whereas the value obtained using hypochlorite alone was 10 ppb, which could be improved to 1 ppb using fluorescein as sensitizer. All systems (except that using the sensitizers) gave luminescences having the same spectra, with maximum intensity at 450 nm.

The emissions were obtained by injecting 0.5 ml of oxidant and catalyst rapidly into a test tube containing 1 ml of sample and buffer, and measuring the emission using a fluorimeter with the light source removed. Under these circumstances, responses such as those shown in Fig. 1 were obtained. Peak height coefficients of variation were about 5%. Ten-fold excesses of thiocyanate or sulphite depressed the emission, but this effect was eliminated by addition of formaldehyde (4 mg ml^{-1}).

DETERMINATION OF SULPHUR COMPOUNDS BY MECA

(a) Direct injection

Molecular emission cavity analysis (MECA) involves the use of a hydrogen-based flame to stimulate emissions from molecular fragments.[4] Because of the low temperature of such flames, the intense emissions achieved must have a chemiluminescent origin. Typical of such emissions are the S_2 and HPO emissions monitored by flame photometric g.c. detectors.

MECA, however, has several additional features to conventional flame emission techniques. In its original form,[4] the liquid sample is injected into a 45-μl cavity at the end of a stainless steel or carbon rod. The cavity is then rotated into a pre-determined position in a hydrogen-based flame, so that emissions generated within the cavity can be measured by a conventional monochromator-detector system.

The cavity heats up at a defined rate when placed in the flame, and the hydrogen-rich flame gases enter the cavity space in a non-turbulent manner. Under these circumstances, a compound injected into the cavity will volatilize (with or without pre-decomposition) into the cavity space, at a temperature characteristic of that compound, and therefore after a characteristic time has elapsed after introduction of the cavity into the flame. If the vapourizing compound contains sulphur, a blue S_2 band emission is produced within the cavity, which can be measured at 384 nm.

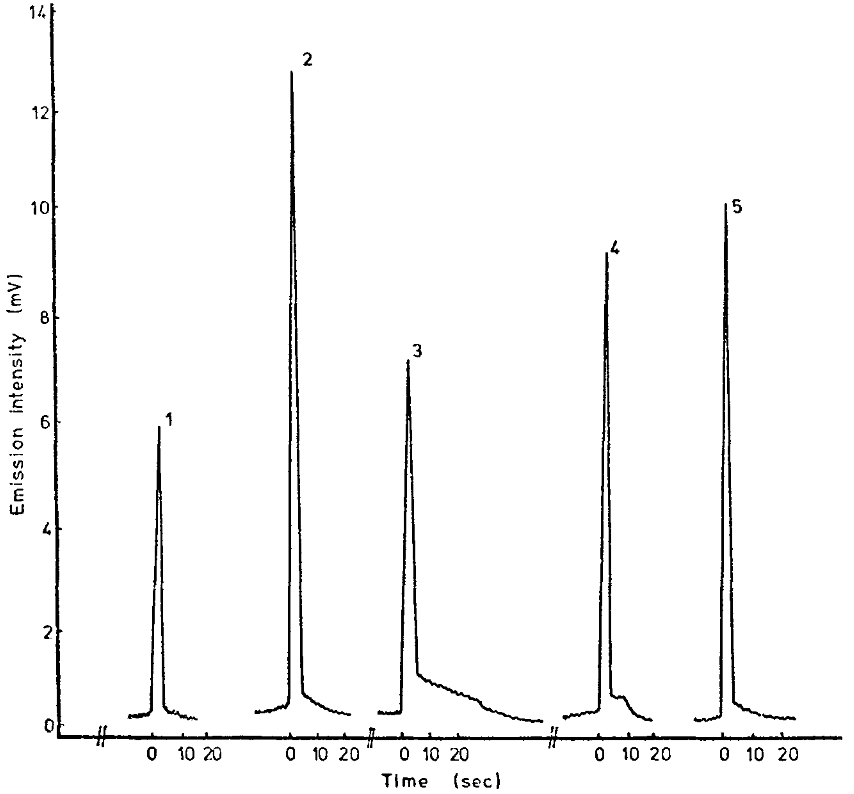

FIGURE 1 Intensity *vs.* time signals from: (1) 0.1 M NaOCl, 10 ppm sulphide, 440 nm; (2) 0.1 M NaOCl, 10^{-3} M fluorescein, 10 ppm sulphide, 515 nm; (3) 1.0 M H_2O_2, 0.25 μg OsO_4 ml^{-1}, 0.01 ppm sulphide, 440 nm; (4) 0.4 M H_2O_2, 750 sigma units ml^{-1} catalase, 0.01 ppm sulphide, 440 nm; (5) 0.4 M H_2O_2, 1.5 purpurogallin units ml^{-1} peroxidase, 0.01 ppm sulphide, 440 nm. 1,2: pH 11.5; 3,4,5: pH 10.0, carbonate buffer.

Because the emission temperature varies with the compound, different sulphates emit at different times. Sulphuric acid, being relatively volatile emits much earlier than copper(II) sulphate, whereas the emission from the much more refractory sodium sulphate is very much delayed (Fig. 2). Thus, although it might be possible to distinguish different solid sulphates in this way, a determination of total sulphate would be very complicated. However, addition of phosphoric acid to the sample ensures that the sulphate response is uninfluenced by cations present, all sulphates giving a response identical to that from sulphuric acid under the same conditions.[5] The determination of ppm levels of sulphate in water samples, therefore, simply involves addition of phosphoric acid (to give a concentration of 0.1 M) and injection of a few μl into the cavity, followed by peak height measurement. Other sulphur anions do not interfere, because their emission occurs well before that from sulphate. It is possible to determine levels below 1 ppm by evaporation of the samples, either in the cavity,[6] or just in a beaker.

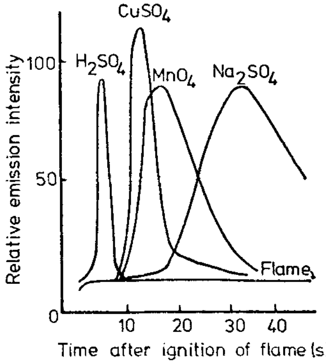

FIGURE 2 Times of MECA responses of some sulphates (arbitrary amounts). Stainless steel cavity with silica liner; flame: 4.5 l H_2 min^{-1}, 6.5 l N_2 min^{-1}.

Sulphonate and sulphate detergents can be measured in almost exactly the same way.[7]

All sulphur anions give characteristic MECA emissions, which occur at different temperatures.[5] Thus, sulphide emits very rapidly, thiocyanate or sulphite, less rapidly, but significantly faster than sulphate. Thus, it is possible to resolve binary[8,9] and some tenary (e.g. S^{2-}–SO_3^{2-}–SO_4^{2-}) mixtures[9] in a single measurement. The response of thiosulphate, however, has 3 peaks covering the region from the sulphide up to the sulphate peak, and thus presents problems of resolution when it is present.

Solid samples can also be introduced into the cavity. Lichen samples, for example, show much more intense (but unidentified) S_2 emissions when they are obtained from urban or industrial areas than from the countryside.[10] Glass-fibre air filters can be used and then introduced directly into the flame by incorporation in a specially-designed cavity, and the responses measured.[11] Work is in hand measuring SO_2 and SO_3 in aerosols in this way.[12]

(b) Volatilization systems

By generating a vapour from the analyte in an apparatus outside the cavity, it is possible to restrict the function of the flame to an emission stimulant. The vapour is then transported to the cavity by a carrier gas such as nitrogen. This has certain advantages, such as better control of selectivity, larger sample volumes and adjustment of the flame condition to give greatest emission intensity, without the need to compromise because of the vapourization/decomposition function of the flame.

Whilst vapourization of sulphide and sulphite is readily achieved by simple acidification,[13] that of sulphate would appear to be difficult. However, by use of the tin-phosphoric acid reagent described by Kiba *et al.*,[14] very effective reduction to H_2S is achieved at 198°C. The sample solution (e.g. 1 ml) is injected into the cold reagent, which is gradually heated up. Emission begins when the reagent reaches 198 C, and the H_2S is carried to the cavity placed in a hydrogen diffusion flame.[15] The sensitivity achieved is much greater than the direct MECA injection procedure, concentrations down to 10 ppb or less being measurable, the limits being set by sulphate contamination of reagents and solvent. The method has so far been applied to water samples, and to measurement of the sulphur content of numerous oils, polyurethane foam, coal and orchard leaves, after oxygen-flask combustion.[15]

If the sample contains mixtures of sulphur anions, these give successive peaks as the acid-reductant heats up. For example, sulphite gives a very rapid response, thiosulphate a delayed response, whereas sulphate is even later. Because the temperature of the volatilization system can be controlled much more readily than that of the cavity, much greater selectivity and resolution can be achieved in this system.

OTHER ENVIRONMENTAL APPLICATIONS OF VOLATILIZATION MECA

Many other species can be converted to gases which give MECA emissions, including the various hydrides,[13,16,17] (AsH_3, SbH_3, H_2Se, H_2Te, SnH_4) all of which give sensitive emissions. Oxygen must also be introduced into the cavity (the oxy-cavity) for As, Sb and Sn, because their emissions arise from their oxides.

Ammonia (or ammonium ion) is readily volatilized by injecting the sample solution on to sodium hydroxide pellets. The ammonia gives a characteristic continuum emission in the oxy-cavity, which allows down to 1 ppm of ammonia, e.g. in effluents, to be measured very simply.[18] The procedure can be extended to nitrate by including Devarda's alloy with the alkali.

Finally, silicon is readily volatilized from a fluoride–conc. sulphuric acid mixture at 180°C into an oxy-cavity, where the blue-white Si0 emission is produced.[19] This allows ppm levels of silicon to be determined or, indirectly, similar concentrations of fluoride. The method has been applied to fluoride in river waters and in toothpaste. It has the advantage over most other methods in that phosphate does not interfere.

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