

Sulphate measurement in organic-rich solutions: Carbonate fusion pretreatment to remove organic interferences

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Abstract

Sulphate measurement using a barium sulphate turbidimetric method in solutions with high concentrations of organic material is shown to be problematic. The organics give background colour, which introduces a positive error to the measured absorption, and inhibit the barium sulphate precipitate, which results in a negative error. A carbonate fusion pretreatment of the sample results in the removal of the organic matter and associated interferences. With this pretreatment, excellent sulphate recoveries were obtained (100%). Rigorous testing of the method shows that reproducible and accurate results are obtainable.

Keywords: sulphate measurement, organic interference, carbonate fusion

Introduction

In a variety of applications of biological sulphate reduction, measurement of sulphate in the presence of elevated concentrations of organic materials is required. Such measurements have proved problematic due to interferences caused by the organic material. This paper investigates the interference of organics in sulphate measurement by standard methods, and proposes modifications to the prescribed methods to overcome these interferences.

Standard Methods (1985) describes four methods for the determination of sulphate in water: Methods 426A, B, C and D. Two of these methods (426A and 426B) involve the formation of a barium sulphate precipitate in hydrochloric acid at near boiling temperature, followed by a period of digestion (>2 h), filtration of the barium sulphate, which is then either dried (426B) or ignited (426A), and the residue weighed. However, both methods are described as being subject to much interference, leading to both positive and negative errors. Interferences include suspended matter, silica, barium chloride, nitrate, sulphide and alkali metals, all of which add to the mass of the dried or ignited residue, or substitute the barium ion with one of a lower or higher molecular weight. Accordingly, these two test methods were rejected for further evaluation.

Method 426D requires the availability of an auto-analyser, which would render it unfeasible unless large quantities of samples were being tested and hence was not investigated further. Method 426C involves the formation of a barium sulphate precipitate in an acetic acid buffer solution, and the measurement of the absorbance of the precipitate using a spectrophotometer at 420 nm wavelength. However, *Standard Methods* (1985) lists colour, suspended matter and organic material as the major interferences. If the organic material and colour can be removed from the sample to allow for the accurate measurement of the sulphate concentration, the method would seem practical and

feasible. Accordingly, a preliminary evaluation of the method was undertaken.

Preliminary evaluation

Method 426C can be used automated with an auto-analyser, and the accuracy of this automated method was evaluated and also compared with a commercially available sulphate test kit (Merck, Method No 14791). A standard sulphate solution (100 mgSO₄/ℓ) was prepared and increasing amounts of sulphate-free soluble organic solution (soluble fraction of methanogenic anaerobic digester effluent, filtered through a 0.45 μm filter paper, S&S ME 25/21) were added to the standard solution and the sulphate concentration measured using both methods, see Table 1. Clearly, for both methods, as the organic concentration in the sample increases, the accuracy of the analysis deteriorates. The accuracy of the test kit was inferior both for the solutions without sulphate present and for the standard sulphate solution without organic matter, and accordingly the test kit version of the method was discarded.

TABLE 1
Sulphate concentrations of two experiments to determine the effects of a sulphate free soluble organic solution on the analysis of a standard sulphate solution (100 mgSO₄/ℓ)

Sulphate concentration (mgSO ₄ /ℓ)	Volume organics added (mℓ)	Sulphate concentration (mgSO ₄ /ℓ)	
		Merck method	Auto-analyser
0	10	112; 83; 42	0; 0; 0
0	20	77; 66; 78	5; 0; 0
100	0	134; 149; 130	103; 101; 100
100	10	108; 132; 152	112; 113; 112
100	20	119; 123; 120	138; 138; 18

Although Table 1 clearly illustrates the interference of soluble organic matter on the accuracy of Method 426C using an auto-analyser, the accuracy of the method for samples without organic interference was encouraging. Also, the method shows

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