# Biological sulphate reduction with primary sewage sludge in an upflow anaerobic sludge bed (UASB) reactor – Part 2: Modification of simple wet chemistry analytical procedures to achieve COD and S mass balances

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## Abstract

The use of the conventional COD method to measure sulphide proved to be problematic due to the loss of hydrogen sulphide ($H_2S$) during sample handling. For calibration of models based on mass balances, and operation of full-scale systems, it was imperative to develop simple wet chemistry analytical procedures for the accurate measurement of parameters like sulphide, COD, alkalinities and VFA in order to monitor BSR systems and achieve 100% COD and S mass balances. Three different analytical methods were investigated to minimise the loss of un-dissociated $H_2S$. Method 1, which is the recommended Standard Methods COD test method, resulted in poor S mass balance (64-75%) due to loss of $H_2S$ during sample handling, mainly vacuum filtration. Method 2, in which 3 drops of 10 M NaOH are added immediately upon effluent sample collection to raise the pH to > 10 and converting un-dissociated $H_2S$ species into the $HS^-$ species resulted in minimal sulphide loss during sample vacuum filtration, dilution, mixing and standing. Method 3, in which a polyelectrolyte is added to the effluent sample to coagulate the organic particles with centrifugation for solid-liquid separation instead of vacuum filtration. Results from Method 3 showed an improvement in the S mass balance with respect to Method 1 - 91% against 75% without a long sample standing period and 88% against 65% with a long sample standing period. However, S mass balance with Method 3 was still relatively low when compared with Method 2 (86 to 91% against 92 to 95%). Therefore, Method 2 was the best simple wet chemistry analytical procedure to accurately measure $S_T$ (= $H_2S$ + $HS^-$) and achieve close to 100% COD and S mass balances. The effects of $S_T$ loss were also investigated on the total and subsystem alkalinities as determined with the 5-pH point titration method. By testing standard solutions with known carbonate, acetate and sulphide species and upflow anaerobic sludge bed (UASB) reactor effluent samples, it was found that the total alkalinity concentration is not affected by $H_2S$ (and $CO_2$) loss as the subsystem alkalinities re-speciate due to a change in pH; and to obtain accurate $H_2CO_3$* alk and volatile fatty acid (VFA) concentrations, accurate sulphide concentrations are required, i.e. those obtained from Method 2.

**Keywords**: biological sulphate reduction, mixed weak acid/base chemistry, titration methods, sulphide, chemical oxygen demand, volatile fatty acids, alkalinity