Most methods for the titrimetric determination of sulfate do not work reliably if interfering divalent cations such as calcium and magnesium are present in the sample. Using the methods described below calcium and magnesium will not interfere and can even be determined in the same analysis.

Greifensee, Zurich -- (SBWire) -- 09/23/2010 -- Several different titration methods are used to determine sulfate content:

a) Titration with barium perchlorate using thorin as indicator. Indication: DP5 Phototrode™ at 555 nm (colorimetric electrode)
b) Titration with barium chloride. Indication: Ba ISE (ion selective electrode)
c) Titration with barium perchlorate. Indication: Pb ISE (ion selective electrode)
d) Titration with lead perchlorate. Indication: Pb ISE (ion selective electrode)
e) Titration with barium chloride. Indication: InLab710 (conductometric electrode)

All these methods work very reliably as long as no interfering divalent cations (e.g. calcium, magnesium) are present in the sample. These must first be removed using a strongly acid ion exchanger, which of course involves more work.

The following article describes a method for sulfate determination in which cations like calcium or magnesium do not interfere and can even be determined in the same method.

Sulfate determination with the Ca ISE

Principle
The basic principle for the determination of sulfate using the calcium ISE (Ca ISE) is really very simple. Sulfate present in the sample is precipitated with an excess of barium chloride at pH 4. The barium still present in the solution after complete precipitation of the sulfate is then back titrated at pH 10 using EDTA and a Ca ISE.

If the sample also contains calcium and/or magnesium ions, the method takes advantage of the fact that the Ca ISE is sensitive to barium and calcium and to magnesium. Since all three cations form complexes at pH 10 with EDTA, they can be analyzed alongside one another.

If the sample does not contain magnesium, the direct method can be used; otherwise the two-step method is necessary.

The direct method
The sulfate in the sample solution is precipitated with an excess of barium chloride at pH 4. After the solution has been adjusted to pH 10, the excess barium is back titrated using EDTA and the Ca ISE. If calcium is present in the sample, the EDTA complexes preferentially with calcium and then with barium.

The resulting titration curve therefore exhibits two separate jumps. The evaluation directly yields the sulfate and
calcium content of the sample.

If magnesium is also present, the direct method cannot be used. The difference in the bonding preference of EDTA with magnesium and of EDTA with barium is too small and would lead to wrong values.

The two-step method
In this case, the calcium and magnesium content must first be determined at pH 10 by titration with EDTA using the Ca ISE. Afterward the solution is acidified (pH 4) and the sulfate in the sample is completely precipitated as before with an excess of barium chloride. After the solution has been again adjusted to pH 10, the sulfate content is determined by back titration of the excess barium with EDTA and the Ca ISE.

Important to note (with both methods)
* Precipitation of sulfate with barium chloride must be performed at a pH = 4 because otherwise precipitation is not complete.
* Titration with EDTA must be done at a pH = 10 because otherwise evaluation of the titration curves is difficult and inaccurate.
* Large amounts of precipitated barium sulfate lead to occlusion effects, which result in low sulfate values. To achieve accurate results, we recommend that you use dilute samples (about 0.05 mmol sulfate per sample) and titrant (e.g. 0.025 mol/L EDTA).

The calcium ISE (Ca ISE)
The use of a Ca ISE together with the InLab301 reference electrode has proven to be very reliable for this application. The Ca ISE is ready for use after just two hours conditioning in a 0.01 molar calcium solution.

In the two-step method, one or two potential jumps are obtained in the first titration depending on the magnesium content and state of the Ca ISE. In general, the first jump (magnesium) is difficult to evaluate and is inaccurate. In most cases this can only be done through post-evaluation using LabX software. For this reason, the two-step method described here uses only the second large jump (calcium) from which the total content of magnesium and calcium can be calculated. The potential jump for calcium is about 1000 mV/mL and about 50 mV/mL for barium if a new Ca ISE is used.

With the direct method, the behavior is the reverse; the potential jump for barium is larger than for calcium. Over a longer period of use, the jump height decreases slowly (to about 100 mV/mL for calcium and about 18 mV/mL for barium). After about 500 determinations reliable evaluation is no longer possible. The signal noise is too large and the jump height too small. The Ca ISE can however be quickly and easily regenerated by replacing the membrane module.

Experimental details

Direct method
For samples with an expected sulfate content of about 0.05 mmol but not containing magnesium, the pH was first adjusted to below 4 using 1.0 mol/L HCl. After adding 2 mL 0.1 mol/L barium chloride, the solution was stirred for a further 2 minutes to ensure complete precipitation. The pH was then adjusted to above 10 with a 5% ammonia solution. In the first titration the solution was titrated with 0.025 mol/L EDTA to the first equivalence point (EQP), from which the calcium content was calculated. The second titration to the first EQP with 0.025 mol/L EDTA allowed the barium content and hence the sulfate content to be determined. It turned out that the theoretically added amount of barium (2 mL 0.1 mol/L) could not be used for the calculation of the sulfate content (the added amount of barium less the amount of barium still in solution after the precipitation of
sulfate) because the sulfate values were then about 10% too high. Possible reasons for this are matrix effects or the slow re-dissolution of the barium sulfate previously precipitated during the EDTA titration. To eliminate this effect, a back value was used for the calculation instead of the theoretically added amount of barium. This was first determined for all samples with similar sulfate contents in the following way:

The amount of sulfate expected in the samples is put in a beaker. Afterward, 2 mL 0.1 mol/L barium chloride is added just as in the sample analysis. The amount of barium still present in solution after the precipitation is called the back value and was determined by EDTA titration.

Two-step method
First 1 mL 5% ammonia solution was added to the sample in order to raise the pH to above 10. The solution was then titrated with 0.025 mol/L EDTA to the first EQP, thereby allowing the total calcium and magnesium content to be calculated. Following this the pH was adjusted to 10 (approx. 6 mL). The resulting solution was titrated with 0.025 mol/L EDTA to the first EQP, which allowed the barium and the sulfate content to be calculated. Just as in the direct method, the calculation had to be performed with a previously determined back value instead of the theoretically added amount of barium in order to avoid high sulfate values. In this back value determination a known amount of calcium was also added. This enabled the back value and the titer of EDTA to be determined simultaneously in one titration.

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