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Quantifying acid-soluble sulfates in geological materials: a comparative study of the British Standard gravimetric method with ICP-OES/AES

Quantifier sulfates solubles dans l'acide dans des matériaux géologiques: une étude comparative de la méthode gravimétrique Standard Britannique avec ICP-OES/AES

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ABSTRACT: Sulfates in geo-materials can lead to a range of civil engineering problems. In accordance with BS1377-3:1990 and EN 1744-1:2009+A1:2012, acid-soluble sulfates in soils and aggregates are quantified using gravimetry, whereby sulfates are dissolved in hydrochloric acid and precipitated as barium sulfate. The sample's sulfate mass is determined as a proportion of the precipitate mass. Gravimetry suffers from many error sources, including occlusion of chloride within the precipitate and incomplete precipitate ignition. On testing of aggregates and reagent-grade sulfates, it was found that the error in gravimetry may be ± 0.1 %SO_4^{2-}. The upper sulfate limit for many aggregates is 0.2 %SO_4^{2-}. Determination of sulfates using inductively coupled plasma (ICP) optical/atomic emission spectroscopy was found to be an order of magnitude more accurate than gravimetry. Tests on reagent-grade sulfates showed a reduction in the standard deviation from 69 %SO_4^{2-} (gravimetry) to 8.5 %SO_4^{2-} (ICP). At 0.2 %SO_4^{2-}, error in the ICP method was ± 0.003-0.004 %SO_4^{2-}. ICP is recommended as the standard approach and a method is outlined herein.

RÉSUMÉ: Sulfates en géo-matériaux peuvent provoquer une série de problèmes de génie civil. Conformément à BS1377-3:1990 et EN 1744-1:2009+A1:2012, sulfates solubles dans l'acide dans les sols et les agrégats sont quantifiées par gravimétrie, de sorte que les sulfates sont dissous dans de l'acide chlorhydrique et précipite sous forme de sulfate de baryum. Sulfate de masse de l'échantillon est déterminée en tant que proportion de la masse du précipité. Gravimétrie souffre de nombreuses sources d'erreur, y compris l'occlusion de chlorure dans le précipité et incomplet d'allumage précipité. Sur le test des agrégats et des sulfates de qualité réactif, on a constaté que l'erreur dans gravimétrique peut être de ± 0,1 %SO_4^{2-}. La limite supérieure de sulfate pour de nombreux agrégats est de 0,2 %SO_4^{2-}. Détermination des sulfates par plasma à couplage inductif (ICP) spectroscopie d'émission optique/atomique a été trouvé pour être un ordre de grandeur plus précis que gravimétrie. Tests sur des échantillons de qualité réactif ont montré une réduction de l'écart-type de 69 %SO_4^{2-} (gravimétrie) à 8,5 %SO_4^{2-} (ICP). A 0,2 %SO_4^{2-}, erreur dans la méthode ICP était de ± de 0,003 à 0,004 %SO_4^{2-}. ICP est recommandé que l'approche standard et une méthode est décrite ici.

KEYWORDS: acid-soluble sulfate, gravimetry, ICP.

1 INTRODUCTION

Where sulfide minerals oxidise, low pH groundwater/drainage may develop if acidity is unbuffered, leading to corrosion of metallic and concrete structures such as buried services and foundations. Dissolved sulfates produced by sulfide oxidation may react with cementicious structures causing sulfate attack of various forms. The crystallisation of sulfate minerals such as gypsum within geological materials can lead to an increase in volume. Buildings founded on oxidising pyritic aggregates in which gypsum develops may undergo heave leading to cracking and structural damage (Hawkins 2013). Heave may also occur following lime-stabilisation of sulfur-bearing subgrade due to the development of sulfates (Snedker 1996).

1 .1 *Need for quantification of sulfates by acid-extraction*

Acid-extraction testing for sulfates in geological materials is used for three major purposes:

a) Quantification of sulfates that are partially soluble (e.g. gypsum) or essentially insoluble (e.g. jarosite) in water.
b) Assessment of the sulfate quantity that may be leached during continued ground/surface water replenishment.
c) Application of derived chemical terms, which utilise the acid-soluble sulfate of a material to estimate proportions of other sulfur phases in a sample.

1 .2 *The British Standard "acid-soluble sulfates" test*

Determination of acid-soluble sulfates within geological materials has traditionally been undertaken using gravimetry in accordance with BS 1377-3:1990 (BSI 1999a) for soils or BS EN 1774-1:2009+A1:2012 (BSI 2013) for aggregates (Table 1). The principle steps common to both methods are as follows:

1) Digestion of a dried and crushed sample in 10 % HCl
2) Filtration of the digestion, retention of the filtrate
3) Precipitation of sesquioxides
4) Acidification of the filtrate with HCl
5) Addition of a barium chloride solution precipitating agent to precipitate barium sulfate
6) Maturation of the precipitate and recovery by filtration
7) Ignition of the precipitate within a crucible
8) Determination of the sulfate content in the barium sulfate precipitate as a proportion of the dry sample mass

Table 1. Comparison of British Standard acid-soluble sulfate methods.

Standard	BS 1377-3	BS EN 1744-1
Material type	Soil	Aggregate
Sample mass (g)	2	8
Max. sample grain size (mm)	0.425	0.125
Vol. H_2O (ml)	90	360
Vol. conc. HCl (ml)	10	40
Digestion time (min)	15	15 ± 1
Sesquioxides removal	Yes	Yes
Filtrate acidification	Yes	Yes
Vol. $BaCl_2$ solution (ml)	10	40
Conc. $BaCl_2$ solution (m/v) (%)	5	10
Maturation below boiling (min)	30	30
Maturation time (long term)	Until cool	Overnight
Ignition temp. (°C)	c. 800	925
Max. quantification (% SO_4)	c. 10	c. 20

1 .3 *Limitations of gravimetric determination of sulfate*

Numerous error sources are associated with gravimetric determination of sulfate within a geological sample (Table 2). During the precipitation stage, the barium chloride solution must be added by a rigorous process of slow addition with vigorous stirring at a controlled temperature to prevent precipitation of barium chloride (Czerewko et al. 2003).

Repeatability and reproducibility equations were reported for gravimetric acid-soluble sulfate testing in BS 812-118:1988 (BSI 1999b) and BRE (2000). The studies indicate that at the 0.2 %SO_4^{2-} tolerance for acid-soluble sulfate in aggregates (BS EN 13242:2002+A1:2007 (BSI 2008)), repeat tests on different portions of the same sample at one laboratory are 95 % likely to differ by less or equal to 0.036-0.072 %SO_4^{2-}. Repeats on different portions at different laboratories are 95 % likely to differ by less or equal to 0.17 %SO_4^{2-}.

Table 2. Sources of error in gravimetry. Contribution to precipitate mass: P = positive, N = negative. References (R): 1) BSI (1999a), 2) Blumenthal & Guernsey (1915), 3) Richards & Parker (1895), 4) Rainwater & Thatcher (1968), 5) Little (2009), 6) Harris et al. (2002).

Aspect	Error source	Type	R
Oxides	Incomplete removal of sesquioxides	P	1
Precipitate contamin-ation	Encapsulation of clay colloids & dust	P	2
	Occlusion of Cl^-	P/N	3
	Occlusion of other ions	P/N	4
	Incomplete combustion of filter paper	P	-
Loss of matter	$BaSO_4$ dissolution (acidic conditions)	N	5
	Precipitate loss (wash through filter)	N	6
	Flaming losses during ignition	N	6
	Mass loss during precipitate transfer	N	-
Hydration	Crucible dehydration and rehydration	P/N	-
Weighing	Lack of balance calibration	P/N	-

1 .4 *ICP analysis for quantification of acid-soluble sulfate*

Inductively coupled plasma (ICP) analysis can be used to quantify sulfate. Argon plasma is used to excite atoms and/or ions within a nebulised aqueous sample, causing emission of electromagnetic radiation that permits identification based on an element's characteristic radiation wavelength. Quantification by atomic/optical emission spectrometry (AES/OES) utilises the emission intensity, which is compared to standards. Whilst the cost of the instrument is high, the use of ICP for quantification of sulfate provides a number of benefits over gravimetry:

a) Improved accuracy and precision due to omission of the error prone precipitate formation stage of gravimetry
b) No requirement for the toxic reagent barium chloride
c) No requirement to remove sesquioxides
d) Faster quantification (no overnight maturation required)
e) Very high sulfate concentrations quantified by dilution

Reid et al. (2005) proposed a method of sulfate extraction in accordance with BS 1377-3 and quantification via ICP. The method used a sample mass of 0.8-1 g and an extractant of 100 ml 25 % HCl. Duplicate repeatability was generally <0.03 %SO_4^{2-}. The maximum duplicate difference was 0.21 %SO_4^{2-}. The standard deviation between results for three laboratories was <0.09 %SO_4^{2-}. The method was tested against the BS 1377-3 method and analysis of the results shows that the average standard deviation of 0.25 %SO_4^{2-} is in excess of the maximum acid-soluble sulfate (0.2 %SO_4^{2-}) stipulated for aggregates whilst the average range is over twice the tolerance.

1 .5 *Comparative testing rationale*

Gravimetry is potentially unsuitable for accurate determination of acid-soluble sulfate contents of ≤0.2 %SO_4^{2-}. This study (fully documented in the unpublished PhD thesis of St John (2015)) seeks to quantify the accuracy and limitations of the BS 1377-3 gravimetric test and compare it with ICP, with the ultimate aim of recommending an accurate and repeatable method for acid-soluble sulfate testing of geological materials.

2 MATERIALS AND METHODOLOGY

2 .1 *Gravimetric testing*

To assess the accuracy and precision of the BS 1377-3 gravimetric method as well as the effect of increasing the sample mass, the materials described in Table 3 were tested in accordance with BS 1377-3 (Table 4). Run 4 assessed reagent grade gypsum with six sub-stages of triplicate samples representing sulfate contents between 0.03 and 5.58 %SO_4^{2-}.

Sub-investigations were undertaken to quantify error in BS 1377-3. Ignition tests (4 h at 925 °C) were undertaken on filter papers to determine the residual mass. To assess crucible mass change, pre-ignition tests (10 min at 925 °C) were undertaken. Following desiccator cooling, the crucibles were re-ignited (4 h at 925 °C) and desiccator-cooled, to simulate the BS 1377-3 test. Crucibles were sequentially removed from the desiccator and the rehydration characteristics determined. To investigate its resistance to ignition, reagent $BaCl_2.2H_2O$ of mass 0.05-2.0 g was ignited for 4 h at 925 °C and the mass loss recorded.

Table 3. Materials tested for acid-soluble sulfate using BS 1377-3.

Material	Type	Description	Notes/Source
Clay	Natural	Silty clay	Kimmeridge Clay Formation, UK
Sand	Natural, washed	Fine sand (for construction)	CE marked as ≤ 0.2 % acid-soluble sulfate
Barite	Natural	White crystals	N. Yorkshire, UK
Gypsum	Reagent (artificial)	White powder	$CaSO_4.2H_2O$ (Fisher), quoted purity 99.5 %

Table 4. Summary of BS 1377-3 gravimetric experimental work.

Run	Material	Test portions	Portion mass (g)	Testing & analysis rationale
1	Clay	18	2	Precision analysis
2a	Sand	18	2	Precision analysis
2b		18	20	Error reduction & precision analysis
3	Barite	4	2	Solubility testing & precision analysis
4	Gypsum	18	Various	Accuracy & precision

2 .2 *ICP-AES/OES testing*

To assess the suitability of ICP-AES/OES as an alternative to gravimetric quantification, the extraction methodology of BS 1377-3 was used, followed by the below approach:

a) Pass extraction filtrate through 0.45 µm membrane filter
b) Make filtrate volume up to 200 ml in a volumetric flask
c) Transfer 10 ml of diluted filtrate to an ICP analysis tube
d) Analyse sulfur in the diluted filtrate using ICP-AES/OES
e) Undertake calibrations, blank, drift and dilution corrections to quantify sulfur (mgS/l) in the filtrate
f) Calculate the acid-soluble sulfate content, as a percentage of the sample mass, to nearest 0.01 %SO_4^{2-}.

An experimental run of 18 samples, duplicating that of the gravimetric Run 4 experiment, was analysed at ESG in Bretby, UK using an Agilent 700 Series ICP-OES equipped with a one-piece axial torch. A 10,000 mgS/l standard and several blanks were used to undertake drift corrections.

3 RESULTS AND DISCUSSION

3 .1 *Gravimetric testing*

Testing of the clay determined a mean acid-soluble sulfate content of 0.15 %SO_4^{2-} (Table 5). The standard deviation

(0.043 %SO_4^{2-}) is relatively high at 28.7 % of the mean. A similar standard deviation and relative standard deviation (RSD) of 28.4 % was determined for the sand. For both materials, there is a 95 % certainty that the difference between two values is $\leq$0.13 %SO_4^{2-}. Blank analyses indicate an apparent sulfate content of $\leq$ 0.01 %SO_4^{2-}, for which the results were corrected.

Increasing the mass of the sand test portions by a factor of 10 reduced the standard deviation by a factor of three. The mean sulfate content also reduced by a factor of three. There is a 95 % certainty that the difference between two values is less than or equal to approximately 0.04 %SO_4^{2-}. The blank analysis determined a minor positive error of 0.002 %SO_4^{2-} (apparent), suggesting that precision also improved. The sulfate content for the 20 g portions is closer to that expected for washed sand than that obtained for the 2 g portions.

The mean sulfate content of 0.27 %SO_4^{2-} in the barite-rich sample is primarily accounted for by sulfates other than $BaSO_4$ that exist as impurities in the geologically sourced sample.

Table 5. Summary of gravimetric test results (Runs 1-3).

Run	1	2 (a & b)		3
Material	Clay	Sand		Barite
Test portion mass (g)	2	2	20	2
Number of tests	18	18	18	4
Mean (%SO_4^{2-})	0.15	0.16	0.05	0.27
Minimum (%SO_4^{2-})	0.06	0.07	0.02	0.25
Maximum (%SO_4^{2-})	0.24	0.25	0.06	0.28
Range (%SO_4^{2-})	0.17	0.17	0.04	0.03
Std. dev. (%SO_4^{2-})	0.043	0.046	0.015	0.012
Repeat. limit (%SO_4^{2-})	0.119	0.127	0.042	0.033
Relative std. dev. (%)	28.7	28.4	33.1	4.3
Apparent blank %SO_4^{2-}	0.008	0.010	0.002	0.007

The theoretical acid-soluble sulfate content of each gypsum test portion in Run 4 is approximately 55.79 %SO_4^{2-}. Results show that the test is poor at predicting the ideal sulfate content at low sample mass (Figure 1). The inverse relationship between determined and known sulfate content indicates that error is compounded at low sulfate contents.

If the sulfate contents of the gypsum portions are normalised to 2 g samples, functional relationships between the ideal and the determined sulfate content can be derived. For all 18 results the data appear to fit a linear relationship with an associated high coefficient of determination (R^2) of 0.999. If samples with <0.4 %SO_4^{2-} are examined, relatively poor accuracy at low sulfate content is apparent (Figure 2). The positive intercept highlights the overestimation of sulfate.

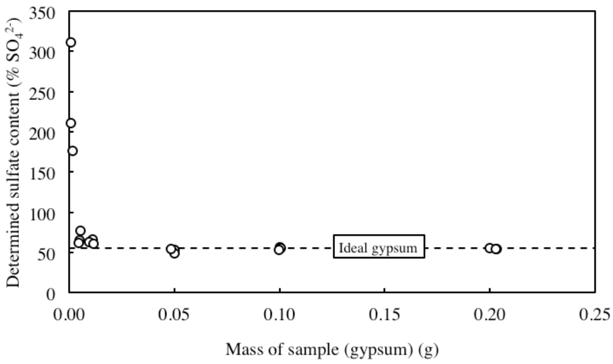

Figure 1. Variation in determined sulfate content with sample mass.

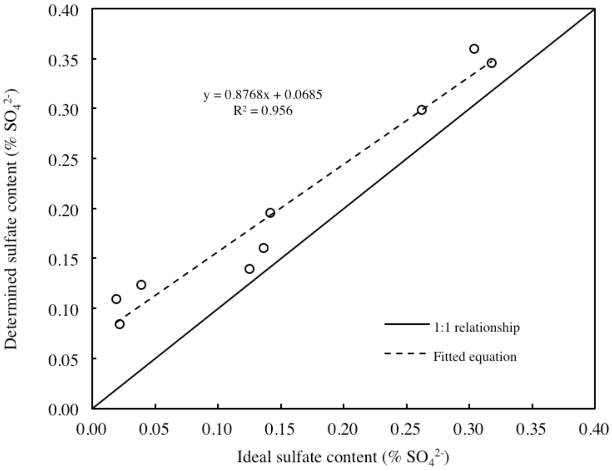

Figure 2. Comparison of the BS 1377-3 determined sulfate content with the ideal sulfate content, for acid-soluble sulfate contents < 0.4 %SO_4^{2-}.

3.1.1 *Assessment of gravimetric error sources*

Pre-ignition tests on crucibles showed a mean mass loss of 0.0027 g or an apparent decrease in the sulfate content by around 0.06 %SO_4^{2-} for a 2 g sample. After 1 h desiccation, ignition of the crucibles (4 h at 925 °C) followed by desiccation showed that post-ignition equilibration in a desiccator is essential for lost mass to be re-gained. Results of Whatman 542 filter paper ashing tests revealed retention of 0.007 % of a 2.4 g paper, or 0.004 %SO_4^{2-} (apparent) by mass of a 2 g sample.

Ignition duration tests on samples with 0.0006-0.6 %SO_4^{2-} showed that on average, an additional 0.006 g was lost between 2-4 h. Negligible further mass loss occurred after 5 h ignition. Mass retention after 2 h ignition could give rise to a 0.12 %SO_4^{2-} overestimate of the sulfate content of a 2 g portion.

Energy dispersive spectroscopy of ignited precipitates showed that Cl^- ions formed the major impurity (< 1% by weight), suggesting that precipitate washing and checking for the absence of Cl^- using the silver nitrate test effectively prevented occlusion. Occlusion of Cl^- adds to the precipitate mass since in most tests there is an excess of barium such that both sulfate and chloride precipitate. For a 2 g sample with a sulfate content of 0.2 %SO_4^{2-}, the error in the ideal precipitate mass is +0.0001 g, equating to a negligible apparent contribution of 0.002 %SO_4^{2-}. Tests on reagent $BaCl_2.2H_2O$ showed that it is partially ignitable after 4 h at 925 °C.

The apparent effect on the precipitate mass and the sulfate content of a 2 g test portion for the error sources described above, in addition to reagent impurities is shown Table 6. Gravimetry is likely to overestimate the sulfate content by an apparent 0.12 %SO_4^{2-} for a 2 g test portion, assuming a low actual sulfate content is present within the geological sample.

Table 6. Quantification of gravimetric error. HCl reported to have $\leq$5 ppmSO_4^{2-}. <2h ppt. ignition assumed, >1h crucible desiccation assumed. *Assumes a sample with 0.2 %SO_4^{2-} content.

Error source	Effect on ppt. mass (g)	Effect on sulfate in 2 g sample (% SO_4^{2-})
SO_4^{2-} in HCl	+0.0001	+0.002
Incomplete ignition	+0.006	+0.12
Filter paper ash	+0.0002	+0.004
Incomplete crucible rehydration	-0.0005	-0.01
Balance error	±0.0002*	Sulfate content dependent
Occlusion of Cl^-	+0.0001*	Sulfate content dependent

3 .2 *ICP-AES/OES testing and comparison*

ICP-AES/OES testing of the gypsum samples was in agreement with the ideal sulfate contents (Table 7). Blank analysis recorded an apparent sulfate of < 3 $mgSO_4^{2-}/l$, corresponding to an apparent sulfate content of < 0.03 $\%SO_4^{2-}$ for a 2 g sample.

The mean acid-soluble sulfate content determined was 58.73 $\%SO_4^{2-}$, 2.93 $\%SO_4^{2-}$ higher than the ideal sulfate content. The standard deviation was eight times lower and the relative standard deviation over five times lower, than the equivalents for gravimetry.

Although an apparent inverse relationship between determined sulfate content and known sulfate content (or gypsum sample mass) exists, error is much reduced at low sulfate content compared to gravimetry when the sulfate content is normalised to a 2 g sample (Figure 3).

Table 7. Comparison between gravimetry and ICP. DL= detection limit.

Run	4 Gravimetry	4 ICP
Number of tests	18	18
Mean ($\%SO_4^{2-}$)	87.91	58.73
Minimum ($\%SO_4^{2-}$)	49.29	50.00
Maximum ($\%SO_4^{2-}$)	311.64	88.89
Range ($\%SO_4^{2-}$)	262.35	38.89
Std. dev. ($\%SO_4^{2-}$)	69.25	8.54
Relative std. dev. (%)	78.8	14.5
Apparent blank SO_4 ($\%SO_4^{2-}$)	0.010	Below DL

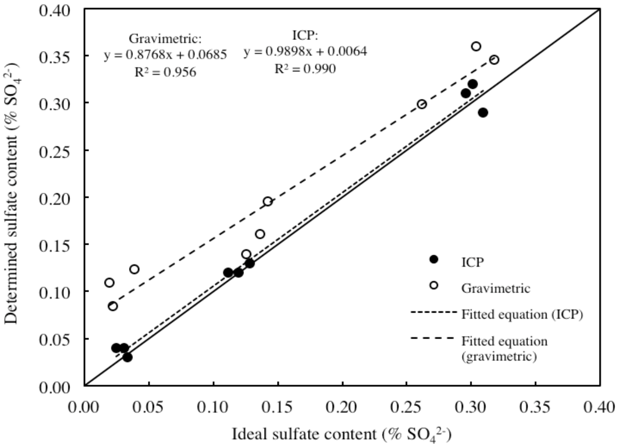

Figure 3. Comparison of BS 1377-3 and ICP for sulfate <0.4 $\%SO_4^{2-}$.

Errors are introduced through dilution of the extract (± 0.0002 $\%SO_4^{2-}$) and transfer of the 10 ml aliquot to the ICP tube (≤ ± 0.0001 $\%SO_4^{2-}$). These errors, when combined with those of the extraction stage, are likely to contribute to an overall error below the reporting of values to the nearest 1 $mgSO_4^{2-}/l$, (equivalent to 0.01 $\%SO_4^{2-}$ by mass of a 2 g sample).

Ignoring labour, sample preparation, provision of capital equipment and tools, safety items, deionisation of water, waste disposal, energy consumption and cleaning, a single gravimetric analysis may cost around £3, with savings made for batches. Savings can be made if Gooch crucibles are used instead of filter papers.

ICP analysis is cheaper at approx. £1 per-sample, but instrument purchase and maintenance costs are high. Higher costs will be incurred for duplicate testing. 5-7 h are required to undertake the BS 1377-3 test on 20 samples. In practice, two days are required, which permits overnight maturation of precipitates. 4-8hrs are required to undertake ICP analysis of 20 samples, however testing can be completed in a single day.

4 CONCLUSIONS

This paper compares the BS 1377-3 gravimetric method for quantifying acid-soluble sulfates with that of ICP-OES/AES. The following conclusions can be drawn:

1) Error in gravimetry is predominantly sourced from incomplete ignition and occlusion of chloride ions. Significant improvements to the BS 1377-3 method can be made by increasing the sample mass, ideally 10-fold; from 2 g to 20 g. This is particularly important for materials with low sulfate content (<1 $\%SO_4^{2-}$).
2) Accuracy in gravimetry was assessed using reagent gypsum to give sulfate contents between 0.03-5.7 $\%SO_4^{2-}$. Comparison of the results with the ideal sulfate content showed poor agreement and overestimation, particularly below 0.4 $\%SO_4^{2-}$. Analysis using ICP to quantify sulfate in the BS 1377-3 extract showed that ICP is capable of accurate determination, even at 0.12-0.13 $\%SO_4^{2-}$.
3) Error in gravimetry for natural samples may be in the order of +0.12 $\%SO_4^{2-}$. Whilst this tends to promote conservative design, it may lead to the misclassification of materials, potential rejection of suitable materials and the inaccurate determination of derived chemical terms.
4) Error in ICP testing was an order of magnitude lower than gravimetry. It is recommended that during revision of the BS 1377-3 and EN 1744-1 Standards, ICP be included as an alternative method for sulfate quantification.

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