



Soil Science Division

ACSAD / ORSTOM

Informative Abstract

Le Centre Arabe Pour l'Etude
Des Zones Arides & Des Terres Seches

- Division Des Sols -

No. 2400

Soufre - Sulfates

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Damas - Septembre 1980

Auteur : xxx / ARIANA
Titre : Dosage des sulfates (methode par turbidimetrie)
Public : Laboratoire de l'ARIANA - D.R.E.S Tunis.
Page/ref : 6 / (5 ref.)

Resume: Les ions sulfates sont precipites par le chlorure de baryum sous forme du sulfate de baryum qui peut etre maintenu un certain temps en suspension en utilisant la gelatine et en gardant les echantillons au frigidaire. L'intensite du trouble est mesure avec un spectrophotometre. Les prises d'essai sont determinees par la teneur (Ca+Mg).

Figure : Courbe d'etalonnage.

Precision: de 0 a 20 meq/l pour une cuve de 1 cm, de 0 a 5ml d'echantillon ramene a 10 ml a 492 nm.

Appareil : Pipette de precision a piston - Spectrophotometre.

Produits : Chlorure de baryum . Gelatine sans sulfate . Sulfate d'amonium . EDTA .

Cles : SULF / COLOR / EAUX / SOLS / MANUEL /

ARIA

Auteur : BATAGLIA (O.C)
Titre : Determinacao indireta de enxofre em plantas par espectrofotometria de absorcao atomica.
Public : Ciencia et Cultura, Vol. 28 - 6 - 1976.

Resume: Methode indirecte de determination du soufre dans les plantes par transformation en sulfate, precipitation au chlorure de Baryum et mesure de l'exces de baryum par AAS a 553,6 nm. Le soufre est mis en solution sur 0.500 gr d'echantillon par 5 ml d'acide nitrique puis 1 ml d'acid perchlorique dans un matra Kjeldahl de 50 ml, on ajoute 20 ml H₂O, 5 ml de BaCl₂ 2500 ppm en milieu HCl 0.1 N. On laisse reposer une nuit, on ajoute 5 ml de SrCl₂ 1,5% on complete a 50 ml. Les conditions de flamme sont etudiees.

Precision: La sensibilite est 1 microgramme/l en flamme N₂O/C₂H₂ contre 4,8 en flamme air / acetylene reductrice qui produit une meilleure stabilite.

Materiel : Spectrophotometrie d'Absorption Atomique - lampe Ba - acetylene.

Reactifs : Chlorure de baryum - sulfate de potassium - chlorure de strontium.

Cles : SULFATE / AAS IND / EAUX / PLANTES.

BATA

Authors : BERTOLACINI (R.J) & BARNEY II (J.E)
Title : Ultraviolet spectrophotometric determination of sulphate, chloride and fluoride with chloranilic acid.
Public : Analytical Chemistry 2 - 30 - 1958. Page 202-204/ref.

Summary: Detailed study of the absorbance of purple acid chloranilate ion (so called "chloranilic acid") is presented within the 310-340 nm range. Analytical principle is the following metal chloranilate + anion A + hydrogen ion \rightarrow acid chloranilate ion (purple) + metal anion salt. Anion A may be chloride, fluoride or sulphate.

Effects of solvent, PH and choice of metal chloranilate are reviewed. Effect of PH is predominant on solvent and PH 4 was selected for sulphate and fluoride ; 0.05N nitric acid solution is selected for chloride. Sulphate is determined at 332 nm with barium chloranilate in 50% ETOH, buffered at PH4 by potassium acid-phtalate and subsequent filtration. Chloride is determined at 305 nm with mercuric chloranilate in 50% methyl cellosolve in nitric acid final medium.

For fluoride PH is adjusted to 7 first, 0.05M potassium acid phtalate is used to buffer at PH4, strontium chloranilate is added, sample is filtered, absorption is measured at 33 nm.

All samples are prealably passed through H cation exchange resin to remove interfering cations.

Tables : - Absorption spectrum of chloranilic acid from 300 to 600 nm.
- Effect of PH on absorption spectra.

Precision: Determination limit 0.06 ppm sulphate / 0.05 ppm chloride / 5 ppm fluoride.

Equipment: UV Spectrophotometer.

Chemicals: ETOH - Methyl cellosolve (barium, strontium, mercuric chloranilate, all home made) isopropanol - chloranilic acid.

Key words: SULPHATE / CHLOR / FLUOR / WATER / RESIN .

BERT

Authors : CARLSON (R.M) - ROSELL (R.A) & VALLEGOS (W)
 Title : Modification to increase sensitivity of barium chloranilate; Method for sulfate.
 Public : Analytical Chemistry 39 - 6 - 1967.
 Page/ref : 688 - 690 (2 ref.)

Summary: An increase in sensitivity of absorption of chloranilate, at 530 nm is proposed.

The reaction of barium chloranilate with sulfate must be carried out in solution of PH= 4 or above the minimize the blank due to the solubility of barium chloranilate. At PH less than 4, acid-chloranilate is formed which correspond to higher concentration of barium chlorinate in solution. The interference of cations produced with chloranilate eliminated by separating these cations by cation ion exchange resin NH_4 .

Figure :- Absorbance of aqueous chloranilic acid as function, of PH (chloranilic acid 8×10^{-4} M).

- Absorbance of chloranilic acid in 50% ethanol as a function of % H_3PO_4 (chloranilic acid 5×10^{-4} M).

Precision: 2 - 100 microeq of sulfate in 20 ml sample standard deviation is 0.04 to 0.75 meq/l and 0.10 a 3.8 meq/l (n = 7).

Appareil : Spectrophotometer (vis), 1 cm cell.

Produits : Amonium chloride . Barium chloranilate . Ethanol . Phosphate buffer ($\text{KH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$) . Cation exchange resin.

Key words: SULF / COLOR / WATER / RESIN /

CARL

AUTHORS : CHAPMAN (H.P) & PRATT (P.F)
Title : Total sulfur in soils.
Public : Methods of analysis for soil, plants and waters, 1961.
Chap. 21, page 184 - 185.

Summary: Two methods are described for total sulfur in soils and waters.

1) Sodium peroxide fusion followed by barium sulphate precipitation and gravimetry. Method is given in full details. Extra evaporation with HF is recommended if the precipitate is suspected to contain silica.

2) Alternative digestion with concentrated perchloric acid is also detailed. Precipitation of barium sulphate in water samples is described.

Tables : no

Range : 10 to 240 mgr sulphate in original water sample.

Precision: Errors from solubility and coprecipitation are minimum if the precipitate is washed quickly and if barium chloride is added slowly in hot diluted HCl solution.

Material : Nickel crucibles - Platinum crucibles.

Chemicals: Sodium peroxide - sodium carbonate - barium chloride - methyl red.
HCL - HF - H_2SO_4 - ETOH - $HClO_4$.

Key words: SULF / SOIL / WATER / GRAVIMETRIC / TOTAL .

CHAP

Auteur : DEDENON (J.M)
Titre : Dosage du soufre total dans les vegetaux: Chap. 1 a 5:
Mineralisation et dosage indirect par emission de flamme du Baryum.
Public : Rapport Annuel de l'Association foret - cellulose, 1972.
Pages : 397 - 408.

Resume:

Deux methodes de preparation sont presentees: par combustion en bombe calorimetrique et par combustion catalytique en fiole de Schoniger, qui donnent sensiblement les memes resultats. Le dosage est effectuee par mesure de l'emission de flamme d'un exces de baryum a 510 nm en flamme air / acetylene (photometre). Le soufre est precipite par une solution 3 meq/l de baryum a chaud, en milieu hydroalcoholique pour obtenir un precipite volumineux.

Tables : Courbe d'etalonnage en photometrie de flamme / comparaison des mineralisations en bombe et en fiole de Schoniger .

Precision: La gamme est 0.5 a 5 mgr pour une prise d'essai de 1 gr. en bombe calorimetrique.

Materiel : Bombe calorimetrique . Fioles de Schoniger . Photometrie de flamme ou Appareil d'Absorption Atomique. Presse a pastille . Oxygen .

Produits : Chlorure de Baryum . ETOH .

Cles : SULF / COLORIMETRIE - AAS / PLANTES

DEDE

Auteur : DEDENON (J.M)
Titre : Dosage du soufre dans les vegetaux: Chap. 6: "Dosage automatique par turbidimetrie du sulfate de baryum".
Public : Rapport Annuel de l'Association - Foret - Cellulose 1975.
Pages : 408 - 421.

Resume:

Mesure en flux continu de la turbidite du sulfate de baryum maintenu en suspension par addition de P.V.P 5 gr/l. L'echantillon est acidifie par l'acide phosphorique a 1%. Le rincage alternatif se fait par EDTA en milieu amoniacal. Le chlorure de baryum n'est introduit que pendant la mesure pour eviter d'encrasser le cuve(15 mm trajet optique). La ligne de base est assez mauvaise a cause de l'alternance des PH alcalins et acides.

Precision: La reproductibilite en 0.1 a 0.2% de l'echelle, soit 00.1 a 00.6% de soufre dans l'echantillon (par rapport a la matiere seche) pour 1 a 12 mgr/l de solution etalon.

Appareil : Colorimetre a flux continu - Electrovamme.

Produits : Polyvinylpyrrolydone (P.V.P) . Chlorure de Baryum .
EDTA .

Cles : SULF / AUTOANALYSE / PLANTES / EAUX /

DEDE

Authors : FRITZ (J) & FREELAND (M.Q)
Title : Direct titrimetric determination of sulfate.
Public : Analytical Chemistry 26 - 10 - 1954.
Page/rof : 1593 - 1595

Summary: Alizarin Red S method for sulfate titration by barium chloride or barium perchlorate in 30% alcoholic solution after ion exchange elimination of interfering cations. Experimental parameters are reviewed. Optimum PH 2.3 to 3.7 (apparent). Barium perchlorate is the best titrant, through all anions gave a 1 to 3% error due to coprecipitation. Two simple procedures (macro and semi-micro are given) titration takes 30 see per sample.

Figure :

Range : Two ranges: - 0.2 to 0.8 millimoles in 10 ml H₂O.
- 2 to 4 millimoles in 45 ml H₂O.

Precision: 0.05 to 0.25% for titration of H₂SO₄ 10 to 50 ml expressed as relative standard deviation.

Material : Ion-exchange column.

Chemicals: Alizarin Red S . Amonium sulfate . Barium chloride .
Barium perchlorate . Cation exchange resin 50-100 mesh .
Magnesium . Acetate . Thorin . H₂SO₄ .

Key words: SULF / VOLUM / H₂O / RESIN / TOTAL /

FRIT

Auteur : GRETHER (C)
Titre : Dosage du sulfate par titrage potentiometrique
Public : Application Bulletin, Metrohm No. 38 f.
Pages : 2 (2 ref.)

Resume: L'excès de chlorure de barium ajoute a la solution est titre avec du complexon III (EDTA sel disodique) a PH $11,2 \pm 0,1$ avec determination potentiometrique du point d'equivalence. Un blanc est fait pour chaque echantillon. Les cations genants sont separes sur resine cationique.

Figure : non

Gamme : Jusqu'a 10 mgr/l sulfate.

Precision: non donnee

Materiel : Potentiographe . Microelectrode combinee universelle, electrode en Tungstene, electrode de reference au calomel.

Produits : Chlorure de baryum - EDTA - NH_4OH
Resine cationique.

Cles : SULF / ELECTROCHEMISTRY / RESINE / WATER /

GRET

Authors : HULANICKI (A) - LEWANDOWSKI (R) & LEWENSTAM (A)
Title : Elimination of Ionic Interferences in the determination of sulfates in water using the lead ion selective electrode.
Public : Analyst 101 - 939 - 1976
Pages/ref: 939 - 942 (12 ref.)

Summary:

Sulfate ions are titrated with lead perchlorate using a Pb-sensitive electrode. The best solvent being 75% methanol. 200 times excess of nitrate does not interfere, at 1/1000M level of sulfate. Chloride is eliminated by cation exchange resin. Calcium produces a negative error suppressed by increasing ionic strength with sodium perchlorate.

Figures : Titration graphs of 0.1 and 0.01 millimoles SO_4 /l.

Range : Lower limit 0.01 millimoles sulfate/l, upper limit not given.

Precision: 2% at 60 mgr/l sulfate in 75% methanol PH 4.0 .

Materiel : PH meter . Recorder . Autoburette . Pb selective electrode . Calomel reference electrode.

Chemicals: Sodium . Perchlorate . Lead perchlorate . Methanol . Cation exchange resin . Perchloric acid.

Key words: SPECIFIC ELECTRODE / WATER / VOLUMETRY / RESIN / SULF / HULA

Authors : KAO (C.W) - GRAHAM (E.R) & BLANCHAR (R.W)
Title : Determination of sulfate in soils as the $^{133}\text{BaSO}_4$
precipitate.
Public : Soil Science 112 - 4 - 1971.
Pages/ref: 221 - 224 (6 ref.)

Summary:

Sulfate is extracted from soils by calcium chloride solution. Extract is centrifuged and passed through cation resin H. Aliquot of eluate is pipetted and 0.002N barium chloride, spiked with ^{133}Ba is added. Precipitate is washed, dried and ^{133}Ba determined by a scintillation counter. Phosphate interference is eliminated by repeated washing.

Table : No

Range : 0 - 10 ppm

Precision: Detection limit 0.3 micrograms for 12 gr of soil and 30 ml extracts. Standard deviation calculated between paired comparison of 24 soil samples was 7.4 microgram. in the range of 10 - 130 micrograms SO_4 per gr of soil.

Material : Centrifuge . Micropipet . Scintillation counter .
Aluminium dishes . Ion exchange chromatography column.

Chemicals: Cationex resin 100 - 200 mesh . BaCl_2 . $^{133}\text{BaCl}_2$.
HCL . MCOH .

Key words: SULF / RADIO / RESIN /

KAO

Authors : KARMIE GALLE (O) & HATHAWAY (L.R)
Title : Indirect determination of SO₄ in water by atomic
absorption.
Public : Applied Spectroscopy 29 - 6 - 1975.
Pages : 518 - 520 (9 ref.)

Summary: Sulfate is precipitated by barium chloride. Barium in supernatant is measured by AAS at 553,5 nm using nitrous-oxyde acetylene flame, with background correction (CaOH absorption). The method is claimed to be twice as much fast as conventional gravimetric procedure.

Table : Comparison of AAS with gravimetric method

Range :

Precision:- 3.5% as r.s.d in the range 70 to 500 ppm (n = 10)
- 16 % as r.s.d in the range 13 to 35 ppm (n = 10)

Material : AAS spectrophotometer - Ba hollow cathod lamp.

Chemicals: Barium chloride.

Key words: SULF / AAS - INDIRECT / H₂O /

KARM

Authors : OGNER (G) & HAUGEN (A)
Title : Automatic determination of sulphate in water samples
and soil extracts containing large amounts of humic
compounds.
Public : ANALYST 102 - 453 0 1977.
Pages : 453 - 457 (10 ref).

Summary: Continuous flow nephelometry of sulphate from soil extracts is presented. Dissolved humic compound are separated by in flow dialysis. Shift in baseline is reported and cured by rinsing with EDTA solution phosphate did not interfere at concentration up to 0.001 N, but iron produced a 10% underestimate of sulphate at 60 mgr/l of Fe.

Tables : Continuous flow diagram - table of sulphate recovery - recorder graph of sulphate standard 2,5 to 100 mgr / l⁻¹ sulphate - sulfur.

Precision: Standard deviation is 0.49 in the range 1 - 100 mgr/l of sulphate - sulfur.

Equipment: Continuous flow colorimeter - dialyses (20 - 35 nm).

Chemicals: Tween 80 - barium chloride - calcium orthophosphate.

Key words: SULPHATE / EDTA / WATER / SOIL / AUTOANALYSE /

OGNE

Author : xxx / ORION
Title : Sulfur dioxide electrode, model 95 - 64.
Public : ORION Research Incorporated.
Page/ref : 1

Summary: Electrode for sulfur dioxide determination. Filtrations and distillations are eliminated. Sulfite and bisulfite are measured by acidifying the sample to convert these species to sulfur dioxide.

The action of SO_2 on the internal filling solution of the electrode produce hydrogen ion which depend on the level of sulfur dioxide in the sample.

Figure : Response of electrode from 0 to 200 mV.

Range : 0.1 to 1000 ppm measured directly in liquid.
Down to 0.02 ppm in air (from a 30 liters sample absorbed in sodium hydroxide and brought to final 25 ml volume).

Precision: Aqueous samples only (0 - 50°C) PH = 1.7 .

Appareil : Ion-sensitive electrode - specific ion meter.

Chemicals: SO_2 buffer.

Key words: SULFUR / ELECTRO / INSTR / WATER /

ORIO

Auteur : xxx / ORSTOM
Titre : Dosage du soufre soluble du sol. Dosage du soufre total.
Public : Roneo ORSTOM / 6 pages.

Soufre soluble

Resume: Le soufre est dose a l'etat de sulfate par complexometrie d'une quantite connue de Plomb II ajoute en exces. L'interference des ions biva-
lents reagissants avec EDTA est calculee par une titration a blanc.

La mise en solution du sulfate se fait a l'acide nitrique 5%. On ajoute un exces de nitrate de Plomb II en milieu ethanol. On dose a PH 10,0 avec EDTA N/50 au noir eriochrome. La precipitation de l'hydroxyde de Plomb est evitee a l'aide du tartrate de sodium.

Soufre total

Deux methodes de mineralisation sont presentees: par fusion oxydante et par mineralisation a l'acide nitrique. La titration se fait comme pour le soufre soluble.

Figure : Schema de dosage . .

Precision:

Materiel : Creuset nickel

Produits : ETOH - NO_3H - EDTA (Na_2) - noir d'eriochrome - NaCl - NH_4Cl - tartrate de sodium - bioxyde de sodium - Nitrate de Pb II - H_2O_2 .

Cles : SULF / GYPS / SOLS / VOLUM.

ORST

Auteurs : xxx / ORSTOM
Titre : Dosage des sulfates par complexometrie.
Public : Roneo / ORSTOM (3 pages).

Resume: Determination complexometrique d'un excès de baryum exactement connu en milieu 50% ETOH a l'aide d'EDTA N/50. Les cations biva-
lents interferants sont doses sur un essai a blanc et les resultats retranches. La quantite d'EDTA necessaire a la titration de l'excès de baryum est determinee sur une gamme etalon de BaCl₂ dans les memes conditions que l'echantillon.

Tables : no

Precision: non donnee

Materiel : titration volumetrique

Produits : Chlorure de baryum - pourpre de phtaleine - rouge de methyle - vert diamine B - amoniaque - EDTA - calcine - ETOH - HNO₃.

Cles : SULF / SOLS / EAUX / TOTAL / VOLUM.

ORST

Authors : PINTA (M) & AL
Title : Indirect determinations of Sulphur, Phosphorus, Silicon, Chlorine, Nitric and Amoniacal nitrogen.
Public : In Atomic Absorption Spectrometry Hilger - London 1974. Chapter 9, page 259 - 260.

Summary:

Sulphur is mineralized and precipitate as barium sulphate. Barium is measured by Atomic Absorption either in the redissolved precipitated or in solution if an excess of barium chloride has been added.

The method is suitable for plant material. Oxidation of sulphur by magnesium nitrate (Anon 1923) is described. Two methods (Cunningham 1962 & Magny 1968) are presented in full length. The first measure barium in the barium precipitate after silica has been insolubilized by HCl and precipitate dissolved in EDTA. Barium is measured at 553,6 nm in strongly reducing Air / Acetylene flame. The second method is based on measurement of excess barium after acidification by HNO_3 1/20.

Tables : No

Range : Lower limit of method II is 0.05% in plant material.

Material : AA Spectrophotometer - Barium Hollow Cathod Lamp.

Chemicals: Magnesium nitrate hexahydrate . Barium chloride . HCl . HClO_4 . EDTA . Potassium sulphate.

Key words: SULF / SOIL / PLANT / AAS - METHOD /

PINT

Author : RAWAJFIH (Z)
Title : Sulfate determination by turbidimetry, a modified procedure.
Public : Riyadh Conference on Methodology of Soil, Water and Plant
Analysis, Riyadh October 1977.
Pages/ref: 2 (1 ref.)

Summary:

Turbidimetric sulfate determination by using the turbidimeter or a colorimeter with blue filter (440 nm). Precipitate is stabilized by gum acacia in acetic acid solution.

Figure : no

Range :

Material : Colorimeter with blue filter (440 nm).

Produits : Nitric acid . Phosphoric acid . Gum acacia .
Acetic acid . Barium sulfate . $BaCl_2 \cdot 2H_2O$. Standard
sulfate solution . Working standard sulfate.

Key words: SULF / WATER / TURBIDIMETRY / MANUAL .

RAWA

Authors : STOFFYN (P) & KEANE (W)
Title : Spectrophotometric micro and submicro determination of sulfur in organic substances with barium chloranilate.
Pub : Analytical Chemistry 36 - 2 - 1964/pages 397-400 (6 ref).

Summary: Sulfur is determined on micro organic samples after combustion in Carius tubes with aqua regia as sulfate with barium chloranilate. Interfering cations are removed by NH_4 cation exchange resin (micro batch system). Resultant chloranilate purple ion absorption is measured at 327,5 nm if sulfur is less than 4 micrograms and at 530 nm for 20 to 100 microgr. 40 times phosphate does not interfere if readings are made at 530 nm and if the sulfur concentration is 20 micrograms.

Tables : Recovery of sulfur from methionine and lipid extracts.

Precision: 0.3 to 100 micrograms of sulfur. Relative error is 2% at 1 microgr. level and 1% at 20 microgr.

Equipment: Micro Carius tube (home made) - micro pipette 270°C oven - micro balance - shaker - centrifuge spectrophotometer.

Chemicals: Double distilled water - nitric acid - HCL - NaCl - Amonium formate - ethanol - formic acid - cation exchange resin 50-100 mesh... chloranilic acid - barium chloride - organic sulfur standard - methionine.

Key words: SULFATE / COLOR / WATER / RESIN / MICRO.

STOF

Auteur : THIEBAUD
Titre : Dosage des sulfates dans les eaux par le perchlorate de baryum et la thiorine.
Public : Methodes d'analyse utilisees a Tel Amara - Liban.
Page : 1 (2 ref.).

Resume: Les ions sulfates sont titres a l'aide d'une solution de perchlorate de baryum 0.005 M. La fin du titrage est indiquee par le virage du jaune au rouge de l'indicateur Thiorine. Le PH est ajuste a 2,5 - 4,0 par de l'acide perchlorique. Les cations sont prealablement elimines par passage sur resine cationique forte. Les ions phosphates sont elimines par precipitation au carbonate de Magnesium. Les ions sulfites sont oxydes en sulfate par l'iode.

Tables : no

Gamme : de 5 a 500 mgr/l en sulfate.

Precision: non donnee.

Materiel : Colonne echangeuse de cations.

Produits : Perchlorate de barium - thiorine - resine cationique forte - ethanol - isopropanol.

Cles : SULFATE / MICRO - VOLUM / RESIN / EAUX .

THIE

Authors : WHITEKER (R.A) & SWIFT (E.H)
Title : Volumetric determination of Sulfate and Analysis of
Pyrites. Application of cation exchange resin.
Public : Analytical Chemistry 26 - 10 - 1954
Pages/ref: 1602 ~ 1605.

Summary: Volumetric determination of sulfate
in solution containing chloride, iron (III),
and bromide.

Solution is diluted so that total cation con-
centration is less than 0.1 N and passed through
H-cation resin at 3 ml/min. Column is washed
by 100 ml dist. water effluent is titrated by
NaOH to PH 7.0. Dextrine and dichlorofluorescein
is added, to pink color (halide en point). Sul-
fate is calculated by difference between hydro-
gen and halide en point.

Figures :

Range :- Up to 0.1 N as cation concentration is tested.
- Pyrite are sample gave 46.7% as sulfur (s.d 0.04).

Precision: at 2.52 meq/l sulfate, averate error is 0.02%,
s.d is 0.12 .

Material : Glass Column 16 mm diam. 22 cm long - PH meter.

Chemicals: Cation exchange resin 18 - 40 mesh . Dextrine . Dichloro-
fluorescein . Ethanol .

Key words: SULFATE / VOLUMETRIC / RESIN /

WHIT