Determination of sulphate by turbidimetry in acid sulphate soil

Dosagem de sulfato por turbidimetria em solos tiomórficos

Enrique Miguel Combatt Caballero[1]*, Víctor Hugo Álvarez V[2] and Andrés Ferreira Dos Santos[2]

[1]Córdoba University, Colombia; [2]Universidade Federal de Viçosa, Brasil *Corresponding autor: ecombatt@hotmail.com

Abstract

The objective has been compare three surfactants in dosage of sulfur available in acid sulphate soils. 12 soil samples were collected in the State of Espírito Santo - Brazil and in Córdoba – Colombia. To evaluate the effect of surfactants in the preparation of 20 ml suspension of reading, has been selected 5 ml of suspension and was added 15 ml of working reagent. The 15 ml had 0.8 g of $BaCl_2$ and the treatments were: 8 mg gum arabic, or 0.15 ml Tween, or 30 mg polyvinyl alcohol. In addition to this, was applied 0.15 ml of HNO_3/l at a concentration 50 mmol, in order that pH of the reading suspensions had been between 3 and 3.3. The sulfur was extracted with $Ca(H_2PO_4)_2$, 500 mg/l P in HOAc 2 mol/l and determined by turbidimetry. For comparison of the surfactants were used three replicates by dosage and the data were analyzed by 't' test, to comparison between two methods was applied statistical test of identity of two methods. It can be concluded that the surfactant gum Arabic showed the best performance in operational terms, but it is also possible to use polyvinyl alcohol for the quantification of $S-SO_4^{2-}$.

Key words: Available sulfur, barium sulfate, gum arabic, surfactants.

Resumo

O objetivo foi comparar três substâncias tensoativas na dosagem do teor de enxofre disponível de solos tiomórficos. Foram coletadas 12 amostras de solos no Estado do Espírito Santo - Brasil e, em Córdoba - Colômbia. Para avaliar o efeito das substâncias tensoativas na preparação de 20 ml de suspensão de leitura, tomou-se 5 ml da suspensão e adicionou-se 15 ml de reagente de trabalho (RT). Os 15 ml de RT teve 0.8 g de $BaCl_2$ e os tratamentos foram: 8 mg goma arábica, ou 0.15 ml tween ou 30 mg álcool polivinílico. Além de disso, foi aplicado 0.15 ml de HNO_3 50 mmol/lt para que o pH das suspensões de leitura ficassem entre 3 e 3.3. O enxofre foi extraído com $Ca(H_2PO_4)_2$, 500 mg/lt de P, em HOAc 2 mol/l e determinado por turbidimetria. Para comparação das substâncias tensoativas de dosagem, se realizaram três repetições por método de dosagem e os dados obtidos foram analisados pelo teste de 't' e para comparação entre os métodos dosagem foi aplicado o teste estatístico de identidade de dois métodos. Pode-se concluir que a substância tensoativa goma arábica apresentou o melhor desempenho em termos operacionais, mas também é possível o uso de álcool polivinílico para dosagem na quantificação de $S-SO_4^{2-}$.

Palavras-chave: Disponível substâncias tensoativas, enxofre, goma arábica, sulfatos de bário.

Introduction

The turbidimetric dosage techniques may have different readings for $S-SO_4^{2-}$ in the same extract. These differences may be caused by the accumulation of precipitates that settle out with high and variable speed, decreasing the possibility that it can be detected with accuracy and precision. Then it is necessary to increase the nucleation rate of the sulfate and also the use of surface-active substances to increase the time for the barium sulphate (Ba) to remain in suspension for quantifying the turbidimetric procedures of this element. According Charoen *et al.*, (2011), the biopolymer-based emulsifiers such as proteins and polysaccharides such as gum arabic, have been shown to be effective in the formation and stabilization of emulsions which are suitable for improving the biocompatibility, the availability and stability of active compounds (Polizelli *et al.*, 2006). Morais *et al.*, (2006) showed that the turbidimetry is an optical technique essentially quantitative based on the attenuation of the incident radiation owed to the scattering of the concentrated particles that are suspended in a non-absorbent medium.

Kliemannee Malavolta (1993) indicate that the technique of turbidemetric determination of $S-SO_4^{2-}$ shows little sensitivity at low concentrations of sulfates and that there is need for improvement of the technical steps for extraction and dosage of $S-SO_4^{2-}$ in soils. The methods most often used for the quantitative determination of $S-SO_4^{2-}$ on soil fertility laboratories are volumetric, gravimetric, turbidimetric, or colorimetric (Tabatabai, 1996; Alvarez *et al.*, 2001). But the concentration of sulfate ions can also be determined by one of three methods, inductively coupled plasma (ICP atomic emission spectroscopy) (Harris *et al.*, 2003). The colorimetric method exhibits favorable characteristics of simplicity, low requirement of instrumentation, robustness and speed. The technique involves the addition of substances or compounds that can form a stable and reproducible suspension to be measured. This is achieved by means of the rate and degree of turbidity formation and improvement of the conditions for suspension viscosity readings. The objective of this study was to compare three surface-active substances in the dosage quantification of Sulphur with monocalcium phosphate in acetic acid by turbidimetry, in acid sulfate soils.

Materials and methods

12 soil samples were used collected at 0-20, 20-40 and 40-60 cm deep. In the state of Espirito Santo - Brazil nine samples were collected (from 0-20 or 20-40 cm in profiles P1, P2, P4 and P5 13578, and from 20-40 cm in P3 profile) and from the Sinú river valley in Córdoba - Colombia, three samples (0-20, 20-40 and 40-60 cm in P6 profile) were collected. The samples were dried in an oven for 24 hours at 40 °C to reduce the oxidation time, homogenized, milled and subsequently passed through 2 mm mesh a sieve (TFSA) for chemical analysis.

In the TFSA fraction ($\leq$ 2 mm) of each soil the following analyzes were performed: granulometric fractions and electric conductivity according to the methods described by EMBRAPA (2006) pH quantified in water in KCl 1 mol/l using a soil:solution ratio 1:2.5. The content of organic carbon compounds (OC) was analyzed via dry combustion in an elemental analyzer (CHNS/O), Perkin Elmer model PE 2400. For potential acidity (H + Al) a $Ca(OAc)_2$ 0.5 mol/l, pH 7 extractor was used, and determined by titration according to the method described by Defelipo and Ribeiro (1991). The cation exchange capacity (CEC) was determined by the NH_4OAc 1 mol/l, pH 7 method, and the available S was extracted with $Ca(H_2PO_4)_2$, 500 mg/l of P in HOAc 2 mol/l (Alvarez *et al.*, 2001) and determined by turbidimetry (Table 1).

Table 1. Characterization of acid sulfate soil samples used in this study.

Profile	Soil sample[a]	CE (dS/m)	pH_{H2O}	pH_{KCl}	H + Al (cmol/cm³)	CTC (cmol/cm³)	OC (g/kg)	S (mg/dm³)
P_1	P_1H1	2.84	3.7	3.5	32.9	47.72	460	762.3
	P_1H2	8.36	3.0	3.0	144.8	160.90	67.5	14 803.5
P_2	P_2H1	2.74	3.0	3.0	37.0	38.45	76.8	3 811.3
	P_2H2	5.57	3.0	3.0	99.7	102.80	319	5 574.6
P_3	P_3Cg	5.88	3.1	3.0	7.4	7.67	10.9	650.5
P_4	P_4H1	1.85	3.0	3.0	33.7	34.63	133.9	2 178.6
	P_4H2	3.41	3.2	3.0	18.4	34.59	62.3	1 789.6
P_5	P_5A	4.38	3.0	3.0	58.0	72.22	54.2	5 849.2
	P_5Cg	1.08	3.1	3.0	16.3	17.03	24.3	1 211.7
P_6	P_6Ap	1.54	4.6	3.2	7.1	39.32	8.6	1 142.6
	P_6Bgy	2.86	3.5	3.2	29.6	56.94	68.4	1 289.3
	P_6CBgy	1.18	3.8	3.2	18.6	35.69	6.4	1 084.4

a.   P1H1 e P1H2/. Profile 1, H1 and H2 horizons, Organosol, sulfate-acid fibric saline soil. P2H1 and P2H2/. Profile 2, horizons H1 and H2, Organosol , sulfate-acid, fibric saline soil. Profile 3, Cg horizons, Gleysol, sulfate-acid, Orthic (Saline) soil. P4H1 and P4H2/. Profile 4, H1 and H2 horizons, tyipical Gleysol, sulfate-acid humic soil. P5A e P5Cg/. Profile 5, A and Cg horizons, Gleysol , sulfate-acid sodium humic soil. P6Ap, P6Bgy e P6CBgy/. Profile 6, Ap, Bg and CBg horizons, typical Gleysol, sulfate-acid, humic soil (Sulfuric Endoaquepts).

Turbidimetric method

The amounts used to prepare 100 ml of working reagent were $BaCl_2$ 4, 5.38 and 8 g; and for the three tensoactive or surfactant compounds (GA) 40, 53.3 and 80 mg -tween 80 (TW) 1, 3.33 and 666 ml and polyvinyl alcohol (PVA) 146.6, 200 and 246.6 mg. The amounts of reagent to form a 20 ml suspension reading correspond to: BaCl 20.6, 0.8 and 1.2 g for the three surfactant compounds: gum arabic (GA) 6, 8 and 12 mg (tween 80 (TW) 0.1, 0.5 and 1.0 ml and polyvinyl alcohol (PVA) 22, 30 and 37 mg. Moreover, as the pH of the reading suspension must be between 3 and 3.3 within each individual method the pH had to be adjusted by testing different amounts of HNO_3, 0.5, 1.5, 2.03 ml at concentrations of 25 and 50 mmol/l to prepare 100 ml of working reagent solution.

Finally, the times for precipitate formation, after adding 15 ml of working reagent containing $BaCl_2$ was determined, and the amount of each surfactant compound and the concentrations of $S\text{-}SO_4^{2-}$, from the points of the curve plus water to complete 20 ml of reading suspension. The points of the curve were composed by 0, 0.3, 0.6, 0.9, 1.2, 8 and 10 mg/l of $S\text{-}SO_4^{2-}$. Then it was determined that between 45 min and 1h the greatest precipitate formation is presented.

In the second stage, once defined the quantities of reagents needed to prepare 20 ml of reading suspension and the reading time, 5 ml of suspension (extractor/soil) were taken and 15 ml of working reagent (RT) were added. The 15 ml of RT contained

0.8 g of BaCl$_2$ and treatments, containing surfactant substances, the dosages being: 8 mg gum arabic, or 0.15 tween ml or 30 mg polyvinyl alcohol. In addition to this, in the preparation of 15 ml RT should have 0.15 ml HNO$_3$ 50 mmol/l, corresponding to 1.5 ml HNO$_3$ 50 mmol/l to prepare 100 ml of RT. These amounts of HNO$_3$ are required in order to maintain the pH of the reading suspensions between 3 and 3.3.

Data from three replicates per method, obtained with the three surfactant substances were subjected to analyses of variance and 't' tests (SAS-Statistical Analysis System) (SAS, 2007). In addition, to compare between dosage methods, the statistical identity test of two methods proposed for Leite and Oliveira (2002) was applied. According to Leite and Oliveira (2002) two methods are considered to be statistically equal, while, simultaneously, after adjusting the linear regression $\hat{y} = \beta 0 + \beta 1 X + e$, $\beta 0$, $\beta 0$ equals to zero and $\beta 1$ equals to 1, with the value of r near 1. However the statistical 't' tests $\beta 0 \neq 0$ or $\beta 1 \beta 1 \neq 1$, that is, the procedure does not test whether $\beta 0 = 0$ while $\beta 1 = 1$. To resolve this problem, a modified statistical 'F' that tests simultaneously if $\beta 0 = 0$ at the same time as $\beta 1 = 1$ through hypothesis H0: $\beta' = [0\ 1]$.

In addition to the 'F' test, it is important to assess the accuracy of the alternative method compared to standard method, by means of the average error quantification. Wanting to see if the error is significant, the 't' statistics was used. In this case, the 't' being calculated <0, 't' tabulated for n - 1 degrees of freedom, the hypothesis ($H_0: \bar{e} = 0$) that the average error is equal to 0 is accepted. Based on this information, a decision rule was followed to test the hypothesis of identity between two methods (Table 2).

Results and discussion

It is noteworthy, for example, that in the laboratory experimentation phase it was not observed the formation of high turbidity in the surveyed suspensions. This is a positive aspect, given that the reading suspension can present colloidal compounds which could act as primary nuclei and introduce high decantation. To compare the surface-active substances, it was decided in this study to present the results in mg/dm of soil.

Table 2. Decision-making rule to compare between dosage methods.

Case	F(H$_0$)	t$\bar{e}$	r	Decision G.A.[a] vs TW[b]	Decision GA vs PVA[c]	Decision PVA vs TW
1	ns	ns	$r \geq (1-\|\bar{e}\|)$	GA = TW	GA = PVA	PVA = TW
2	ns	ns	$r \leq (1-\|\bar{e}\|)$	GA ≠ TW	GA ≠ PVA	PVA ≠ TW
3	ns	*	$r \geq (1-\|\bar{e}\|)$	GA ≠ TW	GA ≠ PVA	PVA ≠ TW
4	ns	*	$r \leq (1-\|\bar{e}\|)$	GA ≠ TW	GA ≠ PVA	PVA ≠ TW
5	*	ns	$r \geq (1-\|\bar{e}\|)$	GA ≠ TW	GA ≠ PVA	PVA ≠ TW
6	*	ns	$r \leq (1-\|\bar{e}\|)$	GA ≠ TW	GA ≠ PVA	PVA ≠ TW
7	*	*	$r \geq (1-\|\bar{e}\|)$	GA ≠TW	GA ≠ PVA	PVA ≠ TW
8	*	*	$r \leq (1-\|\bar{e}\|)$	GA ≠ TW	GA ≠ PVA	PVA ≠ TW

a. = Gum arabic; b. = Tween 80; c. = Polyvinyl alcohol, ns e * denote not significant and significant respectively (P < 0.05). From: Leite and Oliveira (2002).

Table 3. Obtained results after comparing surfactand substances and application of identity test.

Case	Equations	R^2	F(H0)	tē	r	Decision
G.A vs. TW	$\hat{Y} = -177.930 + 0.9485x$	0.96	ns	*	$r \leq (1-\lvert \bar{e} \rvert)$	G.A. ≠ TW
G.A vs. PVA	$\hat{Y} = 94.064 + 0.9827x$	0.98	ns	ns	$r \geq (1-\lvert \bar{e} \rvert)$	G.A. = PVA
PVA vs. TW	$\hat{Y} = -288.09 + 0.9672x$	0.99	*	*	$r \geq (1-\lvert \bar{e} \rvert)$	PVA. ≠ TW

G.A. = gum arabic. TW = Tween 80. PVA = polyvinyl alcohol, ns e * denote not significant and significant respectively (P < 0.05). From: Leite and Oliveira (2002).

It was determined that the average content of $S-SO_4^{2-}$ obtained with the three surfactant substances showed similar values, since the variation in the content of $S-SO_4^{2-}$ in gum arabic (G.A.) and in (TW) were 354.91 mg/dm, G.A. and polyvinyl alcohol (PVA) 41.2 mg/dm and between TW and PVA and 396 mg/dm. These results demonstrate that the three surfactant substances form a stable suspension that avoids the presence of colloildal solutions that could act as primary nuclei and consequently reduce the possibilities of presenting decanted $S-SO_4^{2-}$ in the reading suspension. With respect to the pH of the reading suspensions, it was found that it presented a pH between 3.10 and 3.17, that adjusts to the range of 3.3 and 3 required to increase the precipitation of $S-SO_4^{2-}$ and Ba^{2+}, in addition, to reducing the error in the quantification of the element.

Comparisons among the surfactant substances

For this verification we applied the test of identity between analytical methods (Leite and Oliveira, 2002) considering the surface-active substances by pairs and verifying the equation that explains the relationship between the contents obtained by the reactants (Table 3).

When the substances (Table 2) using gum arabic and tween 80 and tween with polyvinyl alcohol are compared, the identity test showed that are different, meaning that there are differential effects in the surfactant substances tween and polyvinyl alcohol in relation to the surfactant substance that uses gum arabic, presenting

systematic errors ($\beta_0 \neq 0$), and the differences between the methods did not occur at random (tē > ta (n - 1)).

When adjusted to simple linear regression the levels of $S-SO_4^{2-}$ extracted with Ca (H2PO$_4$) 2. 500 mg/1 in 2.0 mol/1 of HOAc, using the work reagent with polyvinyl alcohol (alternative method) and the work reagent with Arabic gum (conventional method), the regression obtained was $\hat{y} = 94.064 + 0.9827x$ with $R^2 = 0.9834$. Applying the identity test it was found that the hypothesis of the intercept $\beta_0 \neq 0$ was not significant and that the hypothesis $\beta_1 \neq 1$ was not significant at 5%. The difference between the comparison of the two methods is admitted as a casual (tē < t α (n-1)).

After comparing gum arabic and tween, and tween and polyvinyl alcohol, identity test indicated that the surface-active substances are statistically different. The regressions obtained were: $\hat{y} = -177\ 930 + 0.9485x$, and $\hat{y} = 94,064 + 0.9827x$, with R^2 of 0.96 and 0.99. The intercept β_0 was significant, therefore $\beta_1 \neq 0$ and β_1 was significant at 5%, indicating that $\beta_1 \neq 1$, in addition to fulfilling the condition of (tē < tα (n-1)) (Table 3).

Conclusions

Using the identity test, significant differences were found between the surfactant substances gum arabic and tween and polyvinyl alcohol and tween 80, but the results estimated by the 't' test indicate that the surface-active substances were similar.

When comparing data obtained from the identity test methods, it was found that the substance of gum arabic shows similar results to those obtained with the surface-active susbstance polyvinyl alcohol.

It can be concluded that the surfactant sustenance gum arabic showed the best performance in operational terms, but it is also possible to use polyvinyl alcohol for dosage quantification of $S\text{-}SO_4^{2-}$.

Acknowledgements

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