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EVALUATION OF SAMPLE PREPARATION PROCEDURES FOR ALUM SLUDGE ANALYSIS AND ELEMENTAL DETERMINATION BY ICP OES

Sena, T.B.M. [abc*] (PG), Machado, R.C. [bc] (R), Nogueira, A. R. A.[c] (R), Ribeiro, C.[b] (R)

[a] Instituto de Química de São Carlos/Universidade de São Paulo, São Carlos, SP, Brazil, Zip Code 780, 13566-590
[b] Embrapa Instrumentação, São Carlos, SP, Brazil, Zip Code 741, 13560-970
[c] Embrapa Pecuária Sudeste, São Carlos, SP, Brazil, Zip Code 339, 13560-970

*e-mail: thaismiqueleti@usp.br

The global increase in water consumption is a growing concern, especially in middle and low-income countries, where socioeconomic development and changes in consumption patterns drive growth. Water treatment plants (WTPs) play a crucial role in transforming raw water into potable water, following established legal parameters. However, the treatment process generates waste, such as alum sludge, characterized by its heterogeneity, influenced by various factors, with the main one being the variation in aluminum sulfate coagulant concentration depend on the water source. During rainy periods, there tends to be increased turbidity, leading to the need for increased coagulant concentration during water treatments. Improper disposal of this waste can cause significant environmental damage.

One possible alternative for managing alum sludge is its use in agriculture and construction. However, the high aluminum content can pose a challenge, causing soil toxicity and impairing plant development. Therefore, understanding the chemical composition of the sludge is essential to determine its suitability for use.

This study evaluated different sample preparation procedures for alum sludge analysis, using microwave radiation and different acidic mixtures (14 mol L^{-1} HNO_3; 3.5 mol L^{-1} HNO_3; Aqua Regia diluted 1:1; inverse Aqua Regia diluted 1:1) for Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, and Zn determination in alum sludge by inductively coupled plasma optical emission spectrometry (ICP-OES, Model 5110, SVDV, Agilent Technologies, Australia). The trueness of the method was evaluated from addition and recovery experiments in two levels, and, for comparison, alum sludge was analyzed using the 3051A USEPA method and the results compared to developed proposed procedures.

The diluted inverse Aqua Regia mixture yielded more efficient recovery results for Al, Ca, K, Mg, Mn, and P elements. Aluminum and Fe were determined by X-ray fluorescence (XRF) in alum sludge. When compared to the concentrations obtained from the proposed method, trueness for Al determination was confirmed, while a discrepancy was observed for Fe. Limits of detection values ranged from 0.53 to 4.71, while the limits of quantification values ranged from 1.75 to 15.7 mg kg^{-1}. The method developed using diluted inverse Aqua Regia and matrix matching in standard calibration solutions was efficient in obtaining satisfactory recoveries for Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, and Zn and proved to be efficient for complex sample analysis as alum sludge.

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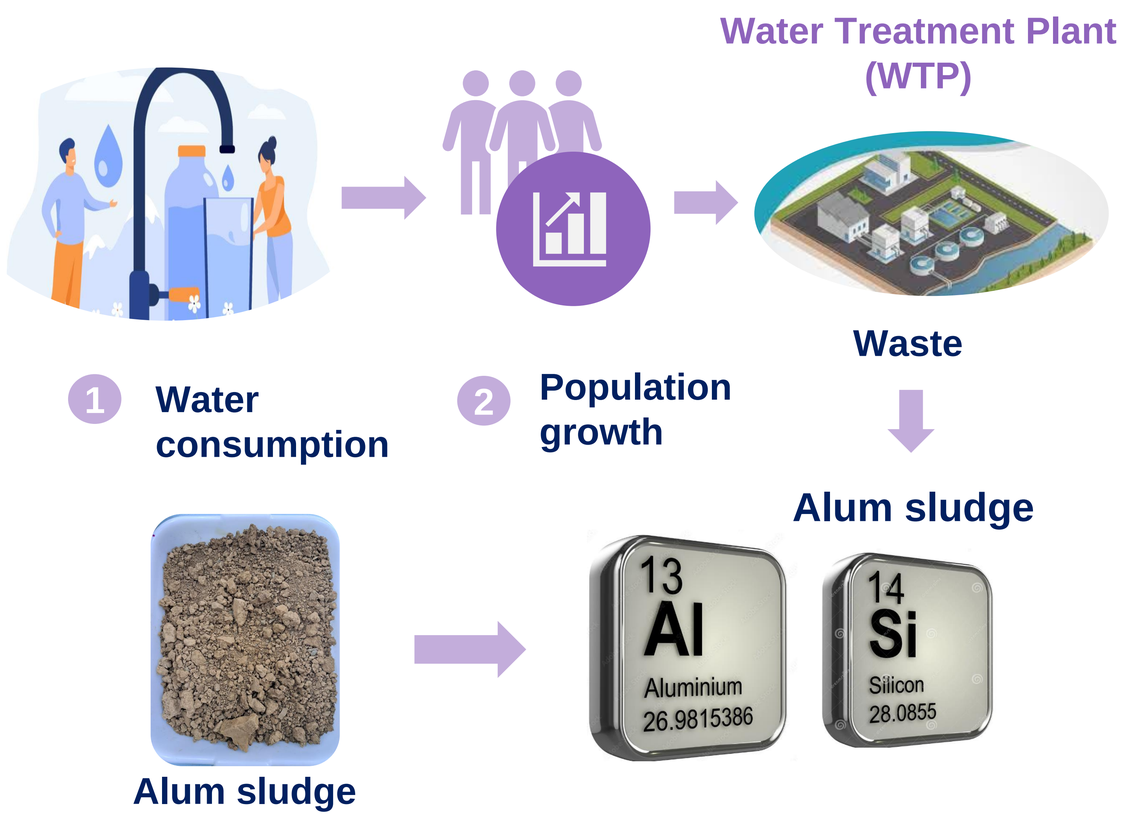
Evaluation of sample preparation procedures for alum sludge analysis and elemental determination by ICP OES

Thais B. M. Sena[1,2,3*], Raquel C. Machado[2,3], Ana Rita A. Nogueira[3], Caue R. Oliveira[2]

[1] Instituto de Química de São Carlos (IQSC-USP), São Carlos, SP, Brazil
[2] Laboratório Nacional de Nanotecnologia para o Agronegócio (LNNA), Embrapa Instrumentação, São Carlos, SP, Brazil
[3] Embrapa Pecuária Sudeste, São Carlos, SP, Brazil
E-mail: thaismiqueleti@usp.br

Introduction

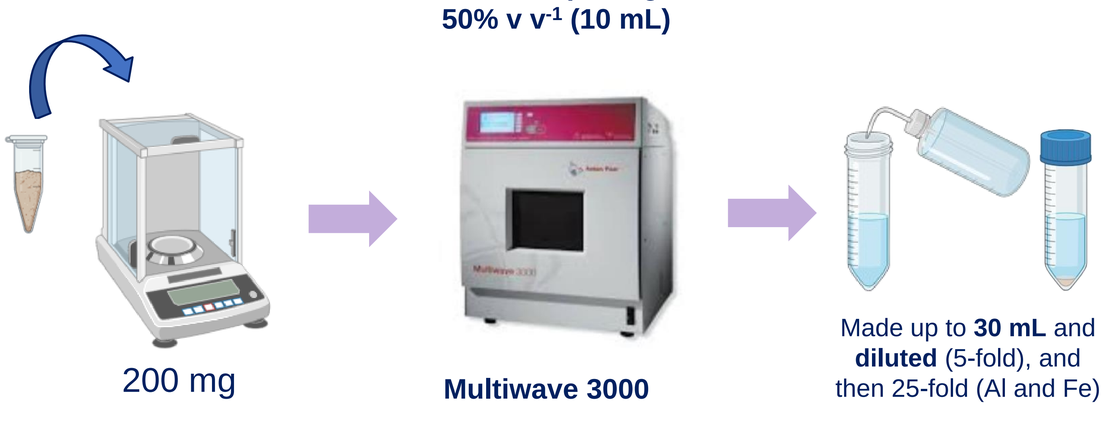


Goal: Evaluate different acid solutions in the sample preparation of WTP sludge using microwave radiation for elemental determination by ICP OES.

Methods

Acid solutions

1. HNO_3 14 mol L^{-1} (10 mL)
2. HNO_3 3.5 mol L^{-1} (10 mL)
3. HNO_3 3.5 mol L^{-1} + H_2O_2 (8 mL + 2 mL)
4. Inverse Aqua regia 50% v v^{-1} (10 mL)



Step	Time (min)	Temperature (°C)	Power (W)
1	20	200	1000
2	10	0	0

ICP OES 5110

The **trueness** of the method was evaluated by comparing the results of the sample preparation procedures with those obtained using the EPA reference method.

Results

Table 1. Concentrations (g kg^{-1}) of Al, Ca, Fe, K, Mg, Mn, Na, P and S determined by ICP OES (mean ± standard deviation, n = 3) in different acid solutions, including EPA method (reference).

Element λ (nm)	Concentration (g kg^{-1})				
	25% HNO_3	25% HNO_3 + H_2O_2	100% HNO_3	50% ARI	EPA
Al (396.152)[a]	97.3±16.5	94.7±8.91	106±1.58	103±3.74	78.6±0.70
Ca (422.673)[r]	1.44±0.25	1.29±0.13	1.59±0.004	1.44±0.23	0.90±0.10
Fe (259.940)[a]	41.2±5.81	41.4±3.77	46.4±0.54	51.2±0.97	52.0±0.20
K (769.897)[a]	3.11±0.68	2.77±0.22	3.23±0.09	3.73±0.26	2.49±0.47
Mg (279.553)[r]	2.94±0.50	2.80±0.25	3.17±0.05	3.49±0.17	1.90±0.10
Mn (259.372)[a]	0.43±0.09	0.42±0.05	0.50±0.01	0.60±0.04	0.48±0.08
Na (589.592)[r]	0.10±0.03	0.11±0.03	0.13±0.001	0.20±0.01	0.13±0.02
P (213.618)[r]	0.89±0.16	0.92±0.11	1.01±0.02	1.02±0.05	1.6±0.02
S (181.972)[a]	0.66±0.08	0.77±0.13	0.80±0.01	0.68±0.06	0.63±0.11

[a] Axial view
[b] Radial view

According to the t-test, the results obtained using a **25% HNO_3** solution showed no statistically significant differences at the 95% confidence level for a greater number of elements, such as **K**, **Mg**, **Mn**, **Na**, **P**, and **S**, when compared to the EPA reference method.

The **25% HNO_3+H_2O_2** acid solution showed no statistically significant differences for **K**, **Mg**, **Mn**, **Na** and **P** and **IAR** acid solution showed no statistically significant differences at the 95% confidence level for **Mg**, **Mn** and **Na**, at the 95% confidence level.

LODs ranging from **1.6** to **220 mg kg^{-1}** and LOQs from **5.2** to **733 mg kg^{-1}** for Al, Ca, Fe, K, Mg, Mn, Na, P and S.

> The LOD/LOQ were calculated considering a 5-fold dilution factor (for Al and Fe, this dilution factor was a 25-fold).

Conclusions

The 25% HNO_3 acid solution proved efficient for preparing alum sludge samples and determining K, Mg, Mn, Na, P, and S using ICP OES, with no statistically significant differences observed for these elements compared to the EPA reference method. Furthermore, the LODs and LOQs are well-suited for alum sludge analysis by ICP OES.

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