

Characterization of Inorganic Solids Present in Brazilian Crude Oil Emulsions Using Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectrometry (EDS): Evaluation of the Effect of Solvents

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ABSTRACT: The characterization and identification of inorganic solids present in Brazilian crude oil emulsions were performed after the application of the ASTM D4807 procedure by scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS). Three modified methods were evaluated to verify the solvent influence on the sediment content of crude oil emulsions with different saline and water amounts: (i) use of a toluene and isopropanol mixture (50% + 50%); (ii) use of a toluene + isopropanol + water mixture (50% + 49.5% + 0.5%); and (iii) use of an additional washing step with hot water of the inorganic solids retained on the nylon membrane filter (0.45 μm). Using the unmodified ASTM D4807 and SEM, different types of solid structures, such as “cubic”, “spherical”, and “star” type, “salt spheres”, and divided solids on the membrane surface, were identified. The main elements identified in the solid structures retained on the nylon membranes were Na, Cl, Ca, Ba, Fe, K, Mg, S, Si, and Sr using the EDS detector. For all proposed modifications of ASTM D4807, a significant reduction in sediment content was observed, probably due to the increase in solubility of the inorganic salts in the solvent mixtures used in these modifications. In modification “i”, a reduction higher than 50% was observed in sediment content for all crude oil emulsions analyzed by this alternative method. For modification “ii”, a reduction higher than 74% in sediment content was observed for the majority of crude oil samples. The results obtained for modification “iii” showed a reduction higher than 82% in sediment content when compared to the unmodified ASTM D4807. After the washing of the membranes with hot water (modification iii), only insoluble salts, such as sulfates of alkaline-earth elements, silica, and iron compounds, were identified on the nylon membrane surface. Modification “iii” can be considered as an alternative method for ASTM D4807, minimizing the crystallization of soluble salts on the nylon membrane surface. Finally, the solvent mixture used in the ASTM D4807 procedure seemed to play a significant role in sediment content determination, due to the crystallization of inorganic salts during the crude oil emulsion analysis.

1. INTRODUCTION

Crude oil is a hydrocarbon-based matrix containing O, N, and S, and it is commonly co-produced as a stable emulsion with water. Inorganic constituents can be found at the oil–water interface, and they originate from different sources, such as the reservoir and corrosion products, and are related to the crude oil emulsion stability. Additionally, a wide range of contaminants, inorganic solids, and brine/water are also present in crude oil emulsions.^{1–3}

The presence of solids, water, and inorganic salts in crude oil is undesirable, because it can cause serious drawbacks for downstream oil, such as fouling of the tank and downstream equipment, corrosion, or catalyst poisoning. In this sense, salts and water may be removed from the crude oil using a desalting process based on electrostatic separation.⁴ However, some inorganic solids (e.g., silicates, aluminum oxides, and carbonates) are not easily separated from the crude oil during the desalting process, causing drawbacks for downstream crude oil.⁵

One of the drawbacks of inorganic salts that are not removed from crude oil is the possibility of HCl formation due to the hydrolysis reaction of chloride salts.⁵ Moreover, according to the literature, the hydrolysis reaction depends on the type of cation present in the salt composition of crude oil emulsions.^{6,7} For crude oil emulsions containing MgCl_2 , for example, a higher amount of HCl is produced at temperatures up to 350 °C when compared with crude oil emulsions containing NaCl or CaCl_2 .^{6,7} On the other hand, the presence of nonextractable organic chlorides was also reported in the literature, and they can react and generate corrosive HCl under suitable conditions.^{8–10}

Hence, the characterization of inorganic salts present in crude oil emulsions is an important task for the petrochemical

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Analytical note

Silicon determination *via* a SiO rotational line using high-resolution graphite furnace molecular absorption spectrometry: A straightforward approach for the analysis of solid samples prepared as suspensions

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ABSTRACT

High-resolution graphite furnace molecular absorption spectrometry combined with samples prepared as suspensions were used for the quantification of Si in geological samples and in spent catalysts used for petrochemical processing. Measurements at the main Si resonance line at 251.6110 nm were proven unfeasible due to the formation of a *quasi*-continuous signal, which resulted in significant memory effect. An alternative was to monitor the fine rotational spectrum of SiO, which allowed memory effect-free measurements. A SiO rotational line centered at 231.9373 nm was selected to carry out quantitative analysis of Si at high percent concentrations in a variety of solid samples. Pyrolysis and vaporization temperatures were evaluated and optimized as 800 °C and 2400 °C, respectively, without the need to use a chemical modifier. Attempts to produce SiO molecules from acidified aqueous standards containing Si were unsuccessful, as the molecule could only be produced from solid samples, likely due to the formation mechanism that involves thermal decomposition of silicates. Hence, solid samples were prepared as suspensions in 0.14 mol L⁻¹ HNO₃. Calibration was performed using a series of suspensions prepared from a gabbro rock certified reference material (CRM), resulting in a limit of detection of 0.5% (m/m). The accuracy of the method was attested by the analysis of several CRM, including rocks, soils and sediments. Solid spent petrochemical catalyst samples were also analyzed and 97–114% recovery was obtained by spiking the catalyst suspensions with a CRM. The good accuracy demonstrated that the formation of SiO is free from matrix effects and highly efficient under the adopted conditions. Overall, the method was proven accurate and consists on a simple and fast alternative to determine Si in silicate-rich samples.

1. Introduction

Silicon is the most abundant element in the Earth's crust, and it can be found in various materials, such as soils, rocks and even in the atmosphere, mostly as particulate matter [1]. Silicon is an important element in the semiconductor industry and it also finds several applications in specialized materials, such as catalysts. In fact, silicon and aluminosilicate-based catalysts are amongst the most important in the petrochemical industry, with application to processes that include cracking reactions, dehydration, isomerization, polymerization, hydrogenation, oxidation and NO_x reduction, amongst others [2]. Hence, quantification of Si is clearly an important task in industrial processes.

Quantitative analysis of silicon can be considered challenging due to the fact that it is a highly abundant element and therefore susceptible to

contamination. Silicon quantification is also frequently preceded by complex pre-treatment of samples [3]. Several instrumental techniques may be used for quantitative analysis of Si, including inductively coupled plasma mass or optical emission spectrometry, atomic absorption spectrometry (AAS), gravimetry, UV-VIS spectrometry, neutron activation analysis and x-ray fluorescence spectrometry [3]. Amongst these techniques, AAS has some clear drawbacks, since there is significant possibility of formation of Si carbides, which are thermodynamically stable and hinder the atomization process. The SiO molecule, in turn, is relatively volatile and may even be vaporized during the pyrolysis stage when graphite furnace (GF) atomization in AAS is used [3–5].

The modern literature on Si determination using AAS is relatively scarce and essentially limited to the quantification of trace levels of the

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Portable dehumidifiers as an original matrix for the study of inhalable nanoparticles in school

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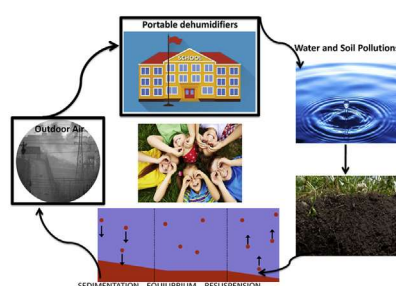
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HIGHLIGHTS

- Investigates on the effect of particulate matter loading on Dehumidifier condensates were conducted.
- Dehumidifier condensates include qualitative material of indoor contaminants.
- 392 nanoparticles and 251 ultra-fine particles recognized resulting a non-target data mining method.
- Particulate surface extent and volume augmented during deposition by condensation.

GRAPHICAL ABSTRACT



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ABSTRACT

Good air quality is documented as a significant factor of social justice. The human health hazards associated with air pollution are not distributed equally across cities; the most vulnerable people are more exposed to ambient air as they commute to work and wait for buses or trains at the stations. Aerosols play important roles in atmosphere quality and the climate; their oxidation at the nanoscale level may possibly increase the reactivity and toxicity of atmospheric particulates. Indoor school environments are characterized by high concentrations of different airborne particulate and gaseous pollutants. The documentation of nanoparticles (NPs), ultra-fine particles (UFPs), and micron-size particle species present in indoor primary schools are an important aspect in the recognition of their influence in respirational difficulties and decreased cognitive progress in children. This work utilizes the study of condensed water, sampled with portable dehumidifiers (PD), to describe NPs and UFPs in the vapor stage of enclosed zones. The acquired extracts were analyzed by advanced electron microscopy techniques. A total of 392 NPs and 251 UFPs were examined in a set of 22 samples acquired in moderately limited or inadequately ventilated indoor areas from several schools. Noting that NPs-related disorders happen at particular places of respirational structure, identification of site-specific NPs accumulation should be anticipated in direction to better verify the corresponding human health outcomes resulting from respirable NPs.

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