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Emulsified systems for metal determination by spectrometric methods

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ABSTRACT

This review summarizes and discusses the preparation and the application of emulsified systems in preparing samples prior to the analytical determination of metals by spectrometric methods. We present and discuss the experimental parameters, such as the choice of surfactant, emulsion-preparation mode and the influences on emulsification processes. We comprehensively summarize published studies covering the application of emulsification as a sample-preparation procedure for the analysis of food, cosmetics and petroleum-based samples. We also describe the main analytical techniques used for the determination of metals by spectrometric methods.

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Contents

1. Introduction

When two immiscible liquids are agitated mechanically, both phases tend to form droplets in the beginning. When the shaking stops, the droplets coalesce rapidly, and the two liquids are separated. This process is spontaneous, but the stability of the droplets can be increased with the addition of a surfactant that acts as a link between compounds lacking affinity by altering the surface tension [1,2].

Surfactants, also called emulsifiers or tensoactives, are defined as molecules or ions that are adsorbed at interfaces [3]. The surfactant contains molecules with an affinity for both oil and water due to the presence of hydrophilic and hydrophobic groups. These compounds have two main functions in the formation of emulsions:

(1) to orient at the interface, decreasing the interfacial tension between oil and water, allowing the formation of the emulsion with little expenditure of energy; and,
(2) to form a film or barrier around droplets with the dispersed phase being stabilized against coalescence [4].

Surfactants have the ability to modify some properties of the system to improve the sensitivity and/or the selectivity of the analytical method, and the main features of using a surfactant relate to the formation of organized settings, also known as micellar environments [5]. The micellar environments, such as microemulsions and emulsions provided by surfactants, have been employed extensively in analytical chemistry.

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Although the development of instrumentation has produced advances in many aspects of chemical analysis, in many cases, the instrumentation does not allow the analysis of samples in their original form because the samples may contain interfering species that are incompatible with the analytical equipment. To circumvent such problems, procedures that may include several steps are employed for sample preparation. Sample preparation for analysis can still be considered the Achilles' heel of the entire analytical procedure because these steps are slow and present the possibility of contamination and/or loss of species of interest during sample handling [6].

The advantages attributed to the use of emulsified systems in sample preparation lie in eliminating the need to digest organic material or to use large quantities of organic solvents. When oil is dispersed in water, the system obtained behaves similarly to an aqueous solution, thereby allowing the calibration to be performed with aqueous standards. The use of emulsions can reduce the final content of organic matter, thus reducing the viscosity, but, by maintaining the homogeneity and the stability of the system, making it suitable to be analyzed by spectrometric methods. The emulsification process offers convenience in sample preparation and use of inexpensive materials. Furthermore, compared with the acidic digestion of organic matter, sample emulsification introduces much less external contaminants to the sample, since sample handling and reagent addition are minimized.

The separation into two phases generated from isotropic micellar systems is another application of surfactants in analytical chemistry. This process is used to extract various types of analytes by cloud-point extraction (CPE). In this process, the surfactant above its critical micellar concentration and heated at a particular temperature can be separated into two distinct phases, an aqueous, surfactant-rich phase and another phase containing the extracted analyte [7]. CPE has been applied widely for extraction and/or pre-concentration of inorganic species for subsequent quantification in various samples, such as water, food, biological and environmental samples [8–10]. The phase separation promotes a high concentration factor, providing enhanced sensitivity and improving selectivity [5].

Surfactants have also been used as adjuncts in the preparation of suspensions of samples (a technique known as "slurry sampling"). Slurries of the solid samples are prepared by ultrasonic mixing of finely-ground materials with H_2O_2 or 5% HNO_3 [11]. Surfactants are added to suspensions to act as stabilizers and to help maintain homogeneity. The surfactants may act to decrease tension between the solid particles (which often have hydrophobic characteristics) and the medium, or to change the physical properties of the suspension, such as the viscosity [12,13]. Foodstuffs, such as chocolate powder, milk and baby food, have been analyzed using this technique [14–18].

This review discusses the practical aspects involved in the application of emulsions and microemulsions as methods for preparing samples for subsequent determination by spectrometric methods. We group the samples according to their characteristics in emulsified and microemulsified systems. We present and discuss the choice of surfactants, the preparation mode and the influence of surfactants on the emulsification processes, and the stability of the systems.

2. Emulsified and microemulsified systems

From the conceptual point of view, it is important to differentiate between emulsified and microemulsified systems.

An emulsion is a two-phase system where one phase is dispersed as droplets in the other. The phase present in the form of drops is referred to as the internal phase or dispersed phase, and the phase that forms the matrix in which the droplets are suspended is called the continuous phase or external phase [2].

A microemulsion can be defined in general as an isotropic system, optically transparent, low in viscosity and containing a pseudo-phase or a dispersed phase consisting of droplets of nanometer size in a phase continuously forming a micro-heterogeneous system, although visually homogeneous [19–21].

The two main types of emulsions and microemulsions are oil in water (O/W) and water in oil (W/O). O/W, where the oil is dispersed as droplets in an aqueous phase, is the most commonly used. W/O incorporates the water particles dispersed as droplets in oil. What determines the type of emulsion/microemulsion is therefore the type of emulsifier and the relative amount of each phase [3].

The emulsifying properties of a compound depend on their characteristics, such as molecular weight, hybridization, presence of charge, voltage angle of the compound, dielectric constant, sites of unsaturation, isomerism and rheological factors, such as viscosity. Samples are grouped according to their characteristics. Table 1 lists petroleum-based products, such as naphtha, biodiesel, kerosene, gasoline, jet fuel, crude oil, lubricating oils and asphaltene. Emulsions and microemulsions have also been applied to prepare food samples, such as edible oils, margarine, butter, eggs, and chocolate, and cosmetics (Table 2).

The main properties of an emulsified system that are desirable for analytical purposes are low viscosity and kinetic stability for sufficient time to perform the analysis. These characteristics can be achieved with an experimental design appropriate for the correct choice of formulation and preparation procedure.

3. Stability of emulsified systems

A stable emulsion can be defined as a system in which the internal-phase droplets retain their initial characteristics and remain evenly distributed throughout the continuous phase [20]. Maintaining droplet size and easy redispersion are essential for the physical stability of the system [3]. The challenge when using emulsified systems for sample preparation is that they must be stable for sufficient time to allow the analysis. Table 1 show the reported stability in the studies reviewed, where it can be seen that the reported stability varies from seconds to months.

The physical nature of the barrier formed by the interfacial surfactant determines whether the droplets will coalesce or not. Any agent or factor that destroys or influences the interfacial film can initiate the break-down of the emulsion (phase separation) [20]. The stability of an emulsion or its resistance to cracking depends on a number of factors, such as the type of emulsifying agent, the viscosity of the emulsion that is formed, the specific weight of the phases, the concentration, the age and the amount of agitation [70]. Aspects, such as Brownian motion, thermogravitational height and the Boltzmann factor also play very important roles in the stability of the emulsion, because the coalescence rupturing thin films of the continuous emulsified phase overcomes the critical disjoining pressure and the Ostwald ripening when the diffusion of the dispersed phase through the continuous phase is controlled by solubility. These factors also affect the stability of the emulsions directly [71].

The mechanisms by which the emulsion may become unstable are creaming, flocculation and coalescence. Creaming occurs under the influence of gravity, with the emulsion droplets tending to separate from the body of the emulsion by emerging or precipitating, depending on the specific differences in density between the dispersed phase and the dispersant [2]. Adhesion is reversible flocculation of the droplets as a result of repulsive and attractive forces between the phases. Flocculation occurs in the interfacial film and

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