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Analytical applications of emulsions and microemulsions

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ABSTRACT

Dispersion systems like emulsions and microemulsions are able to solubilize both polar and non-polar substances due to the special arrangement of the oil and aqueous phases. The main advantages of using emulsions or microemulsions in analytical chemistry are that they do not require the previous destruction of the sample matrix or the use of organic solvents as diluents, and behave similarly to aqueous solutions, frequently allowing the use of aqueous standard solutions for calibration. However, it appears that there are many contradictory concepts and misunderstandings often related to terms definition when referring to such systems. The main aim of this review is to outline the differences between these two aggregates and to give an overview of the most recent advances on their analytical applications with emphasis on the potentiality of the on-line emulsification processes.

1. Introduction

The recent publications on dispersion systems in general, reveal rich information related to their stability, characterization, phase behavior and application fields widely documented in books [1–5] and reviews [6–9]. However, according to the analytical literature published so far on emulsions and microemulsions in particular, and based on the new experimental developments, it appears that there are still many contradictory concepts and misunderstandings often related to terms definition and consequently to preparation procedures for specific applications [10]. Probably, due to the empirical background which is considerably widespread among the analytical applications, and because the analytical work is not, in most cases systematic, the basic understanding of emulsions and microemulsions is jeopardized. It is aimed in this article, for the sake of the newcomers in this field, to outline the current knowledge on emulsions and microemulsions and to give an overview of the most recent advances on their applications. For easy reading and understanding, this review was divided into three sections. The first, gives some definitions and concepts clarification about coarse emulsions, mini- or nanoemulsions and microemulsions including their preparation, formulation and characterization. The second section, resumes recent applications, with emphasis on trace elements determination by atomic spectrometric (AS) methods. Finally, the third section is dedicated to comprehensive remarks and future trends, underlying the on-line emulsification processes developed so far for analytical purposes.

2. Emulsions, nanoemulsions and microemulsions: general aspects

2.1. Coarse emulsions

A coarse emulsion is a kinetically stable system, obtained by the dispersion of one liquid (dispersant) into another (dispersion media or continuum phase), where each liquid is immiscible or poorly miscible in the other, e.g. oil and water [1–3]. The emulsions obtained could be oil in water (O/W) if oil droplets are dispersed in water or water in oil (W/O) if water droplets are dispersed in oil. The droplet size is typically between 0.5 and 50 μm. In consequence, emulsions have a cloudy appearance due to the Tyndal effect; the phase interfaces scatter light that passes through the emulsion thus their basic color is white.

In general, emulsions behave as metastable colloids, exhibiting flocculation (clustering of individual dispersed droplets together), coalescence (merging of two or more droplets during contact to form a single larger droplet), creaming (migration of one of the substances to the top or the bottom, depending on the relative densities of the two phases) and breaking (complete separation of the dispersed phase from the liquid in which it is suspended due to large difference in densities), as a result of droplet interactions.

As thermodynamically unstable systems, emulsions do not form spontaneously; manual or mechanical stirring of the ingredients using centrifugation or agitation is necessary. Their surface area and interfacial tension are low (Table 1). The free energy of emulsion formation is greater than zero ($\Delta G > 0$) and as such will show a tendency to break into its two components. The physical degradation of emulsions is due to the spontaneous trend toward a minimal interfacial area between the dispersed phase and the dispersion medium [11].

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Table 1
Some characteristics of emulsions, nanoemulsions and microemulsions.

Parameter	Microemulsion	Nanoemulsion	Emulsion
Formation	Spontaneous	Ultrasonic and high pressure homogenization	Mechanical or manual agitation
Stable	Thermodynamically	Kinetically	Kinetically
Droplet size (μm)	0.01–0.10	0.05–0.50	0.5–50
Appearance	Transparent	Transparent or opaque	Opaque (cloudy)
Surface area ($m^2\ g^{-1}$)	High (200)	Moderate (50–100)	Low (15)
Interfacial tension	Ultra low	Low	Low
System type	W/O, O/W and bicontinuous	W/O or O/W	W/O, O/W or W/O/W and O/W/O
Surfactant concentration	High	Moderate	Low
Co-surfactant type	Short chain alcohol	Long-chain alcohol	None

To enhance the kinetic stability of such a system, emulsifiers (products that contain a molecule with both, polar and non-polar structure) are usually added to the oil–water mixture, thus the stability of emulsions may be engineered to vary from seconds to years depending on application. Complex or multiphase emulsions can also be obtained by mixing a secondary emulsifier with the primary emulsion: e.g. a complex W/O/W emulsion is obtained by mixing a W/O emulsion with a hydrophilic surfactant, while mixing an O/W emulsion with a lipophilic surfactant, an O/W/O complex emulsion is obtained. Bancroft's rule states that the emulsion type will depend more on the nature of the emulsifying agent than on the relative proportions of oil/water present or the methodology of preparation [12]. The phase in which the emulsifier is more soluble constitutes the continuous phase. Thus, emulsifying agents that are preferentially oil soluble form W/O emulsions and vice versa. Respectively, more polar or non-polar the oil phase, the more hydrophilic or lipophilic the emulsifier should be. The most widely used emulsifying agents to stabilize emulsions are the surfactants (surface active agents). Each surfactant must have a hydrophilic group (usually a polyhydric alcohol or ethylene oxide) and a lipophilic or hydrophobic group (usually a fatty acid or a fatty alcohol).

Surfactants belong to a group of substances that meet certain characteristics like: good surface activity, are able to form condensed interfacial films and their diffusion rates to interface are comparable to emulsion forming time. According to their structure, surfactants are clasified in: anionic (e.g. sodium stearate, potassium laurate, alkyl sulfates like sodium dodecyl sulfate, and sodium sulfosuccinate); nonionic (nonylphenol with ethylene oxide units, polyglycol, fatty acid esters, and lecithin); cationic (quaternary ammonium salts and amine hydrochlorides); zwitterionic/amphoteric (aminoacids, phospholipids, and derivatives of quaternary ammonium compounds) or polymeric and silicone surfactants which could be either of the above [13–15]. According to their type, the molecules of emulsifier are adsorbed at the surface of oil or water droplets, providing a protective membrane that prevents the droplets from flocculating or coalescing. Endogenous materials present in some samples, such as asphaltenes and resins, sufficed to stabilize the emulsions, without the need of surfactant addition. Some aspects and advances on surfactant-free emulsions have been reviewed by Sakai [16]. Preparation methodology involving acoustic emulsification, removal of gas from each phase or utilization of solid particles influence the characteristics of the emulsions obtained. The results are interesting from scientific point of view and help design certain applications with economical and/or environmental requirements since material use is minimized. In order to be effectively emulsified, oils with a certain structure will need surfactants with a specific polar/non-polar character, which is described by two specific parameters, namely the hydrophilic/lipophilic balance (HLB) and the critical packing parameter (CPP). A surfactant is chosen for a certain application mostly by trial and error, although the best way is to learn how to use HLB value which only applies to nonionic surfactants. In other words, HLB is an indication of the surfactant solubility in either phase and has been arbitrarily assigned values between 0 and 20, being 10 the middle point to classify emulsions by type. This concept was developed by Beerbower and Hill [17] assuming that the partial solubility parameters of oil and emulsifier lipophilic tail and of water and emulsifier hydrophilic head are perfectly matched. Its measure is based on molecular weights, following the formula:

$$\mathrm{HLB} = \frac{100}{5} \times \frac{\text{weight of polyethylene oxide chain}}{\text{total molecular weight of surfactant}}$$

Each oily material requires a different strength of emulsifier to ensure the stability of its emulsion. This is referred to as the HLB requirement for that oil. Vegetable oils are the easiest to emulsify, mineral oils are moderately difficult, while silicone oils are the most difficult to stabilize. Matching HLB and the chemical structure of oil and emulsifying agent is an ideal situation. Such information however is only available for a limited number of compounds. Aldrich Materials Science (Sigma–Aldrich catalog) for instance offers a wide variety of nonionic surfactants with a broad range of HLB numbers to help users select correctly the surfactant for emulsions stabilization. Low HLB values indicate an oil-soluble (lipophilic) and higher HLB values are related to more water soluble (hydrophilic) surfactants (Table 2). Blending surfactants (by varying their composition in the mixture) also allows the selection of an optimum HLB for a given application.

CPP relates surfactant molecular parameters like head group area (a), hydrocarbon chain length (l) and hydrophobic tail volume (v) to the shape and size of the microstructure through the formula [18]:

$$\mathrm{CPP} = \frac{v}{al}$$

where $v = 0.027(n_c + n_{methyl})$; n_c is the number of carbon atoms without the methyl group and n_{methyl} is the number of methyl groups and $l = 0.15 + 0.127n_c$. CPP values vary between 0.5 and 3.0.

Table 2 shows the relationship between HLB and CPP values regarding the solubility of surfactant, also called surfactancy, and thus the type of aggregate formed. When the surfactant has equal affinity for oil and water, microemulsions are formed [19,20].

Based on the Bancroft's rule, it is possible to change or invert an emulsion from O/W type to W/O type by inducing changes in surfactant HLB and CPP values. Making the emulsifier more oil soluble tends to produce a W/O emulsion and vice versa. This is accomplished by: (i) altering the order of the addition of the phases (e.g. adding water to oil and emulsifier will produce a W/O emulsion, while adding oil to water and emulsifier, an O/W emulsion is obtained); (ii) variations in the phase volume ratio (e.g. if the oil/water ratio is increased, an W/O emulsion is obtained, and vice versa); (iii) temperature variations and the presence of electrolytes and other additives like alcohols, disrupt the water molecules around nonionic and ionic surfactants respectively, altering surfactant solubility and therefore inducing inversion (e.g. increasing the temperature of a O/W emulsion, makes the nonionic surfactant

Table 2
Surfactant solubility related to HLB and CPP values.

Microstructure type	Surfactancy	HLB	CPP
W/O	More soluble in oil (lipophilic)	4–6	>1
O/W	More soluble in water (hydrophilic)	8–16	<1
Microemulsion	Equal affinity for oil and water	13–18	1

HLB, hydrophilic lipophilic balance; CPP, critical packing parameter.

more hydrophobic and the emulsion could invert to W/O). Emulsion inversion is particularly useful when the final emulsion is subject to specifications that are not attainable with more conventional emulsification methods, as for instance in the case of tiny droplets of very viscous oils [21].

2.2. Nanoemulsions

A mini- or nanoemulsion is a kinetically stable system obtained by shearing a mixture of two immiscible liquids with a surfactant (nonionic or polymeric) and a co-surfactant (particularly a long chain alcohol). They can be transparent (droplet size range of 0.05–0.2 μm), translucent or turbid (droplet size up to 0.5 μm) depending on the droplet radius and the refractive index difference between the droplets and the continuous phase. To produce a transparent nanoemulsion the two refractive indices should match. Such matching is not always possible then the droplet size must be reduced to values below 0.5 μm [22]. Unless adequately prepared and stabilized, nanoemulsions may show an increase in the droplet size and an initially transparent system may become turbid on storage. Thus the nanoemulsions must be stabilized not only against coalescence, but also against diffusional instability by adding a quantity, e.g. 1–8% (w/w) of a highly oil-soluble, water insoluble stabilizing agent like long chain alkanes and long chain alcohols like cetyl alcohol or octadecanol [11]. The alcohols have the tendency to penetrate into the interfacial zone, concentrate at the oil–water interface to form stronger interfacial film, thus increasing the thickness of the surface layer, but decreasing the degree of dissociation of the ionic emulsifier. In most cases, however, nanoemulsions are prepared using nonionic emulsifiers of the ethoxylated type and also polymeric surfactants.

The adequate process of nanoemulsions preparation is accomplished with ultrasonic devices or high-pressure homogenizers which allow the formation of stable small droplets [14,23]. Table 1 lists some characteristics of nanoemulsions in comparison with emulsions and microemulsions. The long-term physical stability of nanoemulsions nearly approaches the thermodynamic stability, like for microemulsions (see below). Nanoemulsions stability is affected by the ratio of the surfactant layer thickness to droplet radius. Spectrometric methods are normally used to monitor the droplet size distribution of nanoemulsions [24]. It is shown that such methodology provides reliable information on droplet size population at the nano-size range. A recent publication reports the optimal nanoemulsion formulation using minimum surfactant concentration with the aim to increase the solubility of the active ingredient and reduce the variations in its bioavailability [25].

Despite the advantages of using nanoemulsions in different fields [14,22–24], their applications have been limited for several reasons: (1) require expensive equipment for their preparation which is reflected in the price of the final product; (2) lack of understanding of the mechanism of production of submicron droplets and of the interfacial chemistry involving the use of specially formulated surfactants and co-surfactants; (3) lack of knowledge on the mechanism of nanoemulsions stabilization. However, this subject is out of the aim of this review, therefore it is not treated in depth here.

2.3. Microemulsions

Microemulsions are optically transparent and thermodynamically stable dispersion systems of at least three components: a polar and a non-polar liquid phase (water and oil respectively), and a suitable surfactant frequently in combination with a co-surfactant such as an aliphatic alcohol [4,5]. The name "microemulsion" derives from the fact that oil droplets in O/W systems or water droplets in W/O systems are small (Table 1). They serve as unique and versatile compartmentalized environments for different kinds of reactions, because the compartment sizes can be altered at will in both the absence and the presence of additives. Even when there are many more components present, for the sake of simplicity, it is convenient to assume the microemulsions as a surfactant/oil/water ternary system. Surfactants facilitate emulsification by reducing interfacial tension and stabilization by introducing double layer forces and/or solvation forces between dispersed particles. Such solution-like systems form spontaneously when the components are brought together in a proper ratio and when the interfacial tension is around 10^{-3} mN m^{-1} [26]. In many respects, microemulsions are small-scale versions of emulsions and in some publications are simply called emulsions [21]. However, as shown in Table 1, microemulsions differ from emulsions in many respects: formation, droplet size (about 500 times smaller), physico-chemical characteristics (e.g. interfacial tension is lower (about 1000 times) and surface area is higher) and appearance (emulsions are opaque and microemulsions are transparent). Additionally, the two main emulsion types (O/W and W/O morphologies), involve the presence of two-phase behavior at equilibrium. Instead, the structure of microemulsion is classified as three distinct types: (i) W/O microemulsion, in which aqueous phase is dispersed in the continuous oil phase; (ii) bicontinuous microemulsion, in which microdomain of oil and aqueous phase are randomly connected with approximately equal volume; (iii) O/W microemulsion, in which oil phase is dispersed in the continuous aqueous phase [1,4,5]. Moreover, emulsions are kinetically and microemulsions are thermodynamically stable. This is because the microemulsions interfacial tension is lowered so that the interfacial energy becomes very small (comparable to or lower than the entropy of dispersion) and thus, the free energy of droplet formation is lower than zero ($\Delta G < 0$) [11]. Another major difference between emulsions and microemulsions comes from the amount of surfactant needed to stabilize the systems and the use of co-surfactant (none for emulsions).

Understanding the surfactants behavior in the presence of water and oil is an important issue for the optimal formulation of a self-organized system. Some specific aspects have been discussed in Section 2.1 although there are several books exclusively dedicated to this matter [13,17,27]. Also, incorporation of another surfactant (blending), co-surfactants or electrolytes into the mixture of water, oil and primary surfactant, provides an additional degree of freedom which enables the adjustment of phase behavior [28]. Addition of such substances is meant to prepare microemulsions with predetermined properties. For that purpose, the optimal concentration of the additives as well as their nature needs to be determined [5–7]. Bancroft rule [12] is also valid for microemulsions and the selection of nonionic surfactants for microemulsions stabilization is based

on their HLB values. However, HLB has certain limitations for practical applications which have been discussed above. Instead, the Hydrophilic Lipophilic Difference (HLD) which should be as closed to 0 as possible has been lately encouraged to be used [5,29,30]. There are certain parameters like salinity (type and concentration of salt added), working temperature, the type of oil or the type and concentration of co-surfactant, which impair the choice of the optimum surfactant. The calculation of HLD is applicable to both ionic and nonionic surfactants.

For nonionic surfactants, the HLD is given by the equation:

$$\mathrm{HLD} = b(S) - K \times \mathrm{ACN} - f(\mathrm{A}) + c_{\mathrm{T}}\,\Delta T + \mathrm{Ccni}$$

where S is the salinity (in g of salt/100 ml of water) and b is a constant (0.13 for monovalent salts like NaCl and 0.1 for divalent salts like $CaCl_2$); ACN is the Alkane Carbon Number in the oil molecule and K is ~0.17; f(A) is a function of the alcohol type and concentration, c_{T} is a coefficient (0.06) describing the effect of a change in temperature; ΔT is the difference between the working temperature and 25 °C. Ccni is the characteristic curvature specific for a given non-ionic surfactant and seem to follow a simple rule depending on the relative sizes of the surfactant heads and tails.

For ionic surfactants, the HLD is defined by a similar equation:

$$\mathrm{HLD} = \ln(S) - K \times \mathrm{ACN} - f(\mathrm{A}) - \alpha_{\mathrm{T}}\,\Delta T + \mathrm{Cci}$$

where the parameters are equally defined, but S has a logarithmic dependency, α_{T} is similar to c_{T} but its value is ~0.01 (smallest dependency on ΔT), and Cci is the characteristic curvature for a given ionic surfactant and it is obtained from a linear correlation with the CPP.

It turns out that theoretically, for HLD = 0 the solubility would be infinite, which in practice is not true because there is a net average curvature (NAC) as there will always be droplets present with certain radii. To be efficiently implemented, HLD must be calculated only for surfactants with long tails and big heads, which provide low Cc and consequently higher solubilization. If a reliable database is available, HLD and NAC could be easily calculated for any system. The website for the HLD-NAC Software package is www.stevenabbott.co.uk/HLD-NAC.html. Most researchers have no access to this software neither have the complete knowledge or not sufficient data to carry on such calculations thus, as for emulsions, the physical stability of microemulsions is indicated by droplet size change and transparency. The optimum formulation of microemulsions prepared by mixing the sample with a surfactant, a co-surfactant and probably other additives can be followed either by looking for the smallest droplet size, the minimum interfacial tension or by three-phase behavior, these phenomena being essentially equivalent [5,6,28]. Co-surfactants such as short chain alcohols are used to facilitate condensed interfacial film formation with a considerable extension of the microemulsion domain in the phase diagram. The co-surfactant together with the surfactant lowers the interfacial tension to a negative value where the interface will expand to form fine dispersed droplets. The presence of large amounts of these substances represents a drawback that can considerably restrict the potential uses of microemulsions for many applications where high solid contents and low surfactant amounts are usually desirable. Therefore, the preparation of microemulsions with as little surfactant as possible that can be diluted with water in all proportions is a major challenge that attracts interest for practical and theoretical reasons [31]. O/W microemulsions are dilutable with water whereas W/O are not and undergo phase inversion when the amount of water increases in the system. This is a simple test generally used to identify microemulsion type.

Addition of electrolytes like sodium ions, lower the hydration of the surfactant polar head (salting-out effect). Thus, at a given temperature, the HLB of the ethoxylated surfactant or its blend is made more lipophilic, which accounts for an increase in the optimum HLB value [5].

In the analytical applications published so far, the ingredients required by the definition of microemulsion were scarcely used [32–36] and only two of them [32,33] followed the minimum droplet size related to phase behavior. The rest accounted for the optimal formation by visual follow-up of transparency and/or by any increase or decrease in the analytical signal with variations in the reagents concentration. Although microemulsion properties are beginning to be satisfactorily understood, especially the droplet structure, large research domains remain to be clarified.

3. Applications

Emulsification has been the subject of extensive research over the last decades. There are numerous examples of applications in: analytical chemistry to improve sample processing for trace elements determination (e.g. oils and fuels); in cosmetics industry to increase products quality (e.g. hair and skin products); in pharmaceutical industry to make medicines with a more appealing flavor, with antimicrobial properties or easier to deliver; agrochemical and food industries by incorporating new ingredients, etc. The products may be solids, pastes or liquids depending on their oil and water proportions and on the additives incorporated during the preparation process. The quality of such products is mainly followed by determining certain chemical elements using specific analytical methods.

3.1. Spectrometric determination of chemical elements using emulsions

The presence of metallic or metalloid species in samples like lubricating and edible oils, fuels (gasoline, diesel or biodiesel) or other petroleum derivatives (naphthas or asphaltene) may come from raw materials (crude oil, soils and crops), may be added on purpose to improve specific characteristics, may be present as a result of the wear of engine lubricated areas or may be transferred during processing, transportation or storage. Other elements like mercury, arsenic, cadmium or chromium need to be determined due to their toxicity and detrimental effect to human health. Whatever the source, the quantification is necessary either to evaluate the quality and physico-chemical properties of the products or to control environmental emissions. These determinations are mainly accomplished by atomic absorption spectrometry (AAS) with flame (FAAS) or electrothermal (ET AAS) atomization, inductively coupled plasma optical emission spectrometry (ICP OES) and ICP-mass spectrometry (ICP MS) as well as chemical vapor generation (CVG) combined with AAS or atomic fluorescence spectrometry (AFS). Table 3 gives some details on selected publications related to chemical elements determined by spectrometric techniques in liquid organic samples like crude [37–39], fuel [40], edible [41–43], lubricating [44–46] and fish-eggs [47] oils, kerosene [48,49], gasoline [49–53], biodiesel [54] and naphtha [55,56] using emulsion sample preparation.

The presence of some elements in crude oil is undesirable because catalysts causes poisoning in the refining process and pipes corrosion during transport and storage. They are usually transferred to the distilled fractions, obviously in significantly lower concentration, degrading the quality and performance of intermediate and end products. Other elements such as aluminum, calcium, chromium, cobalt, copper, lead, magnesium, manganese, molybdenum, nickel, silicon, sodium, thallium, tin, tungsten, vanadium, zinc and zirconium are deliberately introduced as additives in order to promote higher quality properties [57,59]. Trace metals also have

Table 3
Trace elements determination in oils and fuels using emulsion formation procedures.

Sample	Elements	Analytical technique	Sample processing (mixing type)	Calibration	Method validation	DL	RSD (%)	Ref.
Crude oil	V, Ni, S	ICP-OES	Sample diluted in xylene + nonylphenol polyethylene glycol ether (Manual)	Aqueous standards in HNO_3 treated as samples	Certified materials and ICP-OES after sample digestion	0.02–0.6 $\mu g\,L^{-1}$	1–3	[37]
Crude oil	Pb	ETAAS	Sample diluted in xylene + Triton X-100 + water (Ultrasonic)	Aqueous standards in HNO_3 treated as samples	ETAAS after mineralization	0.004 $\mu g\,g^{-1}$	5–20	[38]
Crude oils	V	HR-CS-ETAAS	Sample diluted in xylene + Triton X-100 + water (Ultrasonic)	Aqueous standards in mineral oil treated as samples	Certified materials	0.04 $\mu g\,g^{-1}$	<4	[39]
Fuel oil	V, Ni, Co	ETAAS	Sample diluted in toluene + Triton X-100 + water (Manual)	Aqueous standards in HNO_3	Certified materials	0.07–6.5 $\mu g\,g^{-1}$	<10	[40]
Edible oils	Ag, Al, B, Ba, Bi, Ca, Cd, Co	FI-ICP-OES	Sample + Triton X-100 + water (Magnetic)	Aqueous standards in emulsifier treated as samples	ETAAS after simple mineralization	NR	<5	[41]
Edible oil	Al, Ba, Bi, Ca, Cu, Mg, Mn, Na, Pb, Sn	FI-ICP-MS/FAAS	Sample + Triton X-100 + water (Magnetic)	Aqueous standards in HNO_3 treated as samples	FAAS after simple mineralization	0.33 $ng\,g^{-1}$	2.4	[42]
Edible oil	As, Cd, Hg	CV-ICP-MS	Sample + HCl + Triton X-100 (Manual)	Standard addition of aqueous standards and isotope dilution	ICP-MS after sample mineralization	0.01–0.04 $ng\,g^{-1}$	?	[43]
Lubricating oils	Pb	FAAS	Filtered sample + Tween20 + water (Ultrasonic)	Aqueous standards in Pb-free unused oil	FAAS after sample mineralization	NR	<2	[44]
Lubricating oils	Fe	FAAS	Sample + (HF/HNO_3) + nonylphenol polyethylene glycol ether + water (Manual)	Aqueous standards in Fe-free unused oil	Spectrophotometric after dry ashing	2 $\mu g\,g^{-1}$	1.5	[45]
Lubricating oils	Pb, Cr, Al, Cu, Ni, Fe, Si, Mg	FAAS	Sample + (HF/HCl) + nonylphenol polyethylene glycol ether + water. (Ultrasonic)	Multielemental-organometallic standard	FAAS after dry ashing	NR	0.4–5	[46]
Fish-eggs oil	MeHg, total Hg	CV-AAS	Sample + Tween20 + water (Manual)	Aqueous standards	Recovery tests. ET AAS after mineralization	0.11 and 0.12 $\mu g\,L^{-1}$	2.2-9	[47]
Kerosene	Zn, Mn	FAAS	Sample + H_2SO_4 + Triton X-100 + water (Manual)	Aqueous standards	FAAS after re-extraction in dioxane	NR	NR	[48]
Gasoline, diesel and kerosene	S	ICP-OES	Sample + HNO_3 + Triton X-100 + water (Manual)	Aqueous standards treated as samples	Certified standards and recovery tests	0.72 $\mu g\,g^{-1}$	2.5	[49]
Gasoline	Mo, V	ETAAS	Sample + HNO_3 + CTAB and CPB as surfactants (Ultrasonic)	Aqueous standards in purified gasoline	Recovery tests	0.9 and 4.7 $\mu g\,L^{-1}$	1.2-4.4	[50]
Gasoline	Cu, Mn, Ni, Sn	ET-ICP-MS	Sample + HNO_3 + Triton X-100 (Ultrasonic)	Aqueous standards in purified gasoline	Recovery tests	0.02–0.4 $\mu g\,L^{-1}$	<4	[51]
Aviation gasoline	Pb	ETAAS	Sample + Triton X-100 prepared in HNO_3 (Manual)	Aqueous standards in mineral oil	Recovery test	1.2 $\mu g\,L^{-1}$	5.1	[52]
Jet fuel	Cu, Fe	ETAAS	Sample + Triton X-100 prepared in HNO_3 (Manual)	Aqueous standards in mineral oil	Recovery test	0.50 and 0.46 $\mu g\,L^{-1}$	<5	[53]
Biodiesel	MeHg, total Hg	CV-AFS	Sample + HNO_3 + Triton X-100 + water (Manual)	Aqueous standards treated as samples	CV-AFS after microwave digestion	0.03 $\mu g\,L^{-1}$	<8	[54]
Naphtha	As, Sb	ETAAS	Sample + HNO_3 + Triton X-100 + water (Manual)	Aqueous standards treated as samples	Recovery tests	2.7 $\mu g\,L^{-1}$	<5	[55]
Naphtha	V, Ni, Pb, Co, As, Hg	ICP-MS	Sample + HNO_3 + Triton X-100 + water (Magnetic)	Aqueous standards treated as samples	ICP-MS after sample digestion	0.05–0.7 $\mu g\,L^{-1}$	2–3	[56]

DL, detection limit expressed as $\mu g\,L^{-1}$ or $\mu g\,g^{-1}$ for liquid or solid samples, depending on procedure; NR, not reported in the paper; RSD, relative standard deviation; AVK, aviation kerosene; HR-CS-FAAS, high-resolution continuum source FAAS; SME-FAAS, sequential multielement FAAS; Tween20, polyoxyethylene sorbitan monolaurate; SDS, sodium dodecyl sulfate.

deleterious effects on the flavor and oxidative stability of edible oils [10].

Because of the high viscosity and the high volatility of crude oil and its derivatives, respectively, the samples require some degree of preparation previous to the analytical measurements. The instability and high cost of the organic standards required for calibration and the lack of certified reference materials for most of the samples makes the analysis even more complicated. Most of the spectrometric methods are therefore preceded by dilution or mineralization steps in order to allow easy sample introduction into the atomizers. Such methods present additional inconveniences like time-consuming and troublesome steps for the optimization, signal fluctuations and high noise level [10]. It appears that preparation of emulsions and microemulsions is the method which fulfills all these requirements. The emulsification approach allows access to high sensitivity without requiring acid decomposition and permits the use of stable inorganic standards for calibration. Any potential loss of analyte elements due to volatilization or precipitation during sample processing is eliminated. The probability of contamination is also reduced because sample handling and reagents addition are minimized. Another positive aspect of emulsification relies on the fact that it brings the viscosity of the sample close to that of an aqueous solution, converts the analyte in a compatible form with its introduction in the instrument maintaining its integrity like in the original sample, the overall organic load is reduced and the system can be reconstituted by agitation with no detriment on reproducibility.

The procedure, first introduced by Hernandez-Mendez et al. [44] for the determination of Pb in lubricating oils by FAAS consists in mixing the surfactant prepared in an inorganic acid with the appropriate amount of sample (usually 1% in weight). All these preparations are known as emulsions but have also been called microemulsions, misleading the terms [55]. The sample is kept stable enough time to perform the analysis. FAAS is a well established and accessible technique, less prone to spectral interferences in comparison to other spectrometric techniques but its sensitivity only allows the determination of additives like Na, K, Ca, Mg or Pb and wear metals like Fe, Zn, Mn, Cr, Si, Cu or Al in lubricating oils and kerosene. The sensitivity was not the important issue in these cases, thus the detection limit (DL) was not even reported in most cases (Table 3).

ET AAS and ICP permitted the quantification of elements present in the same type of samples but in lower concentrations (see some characteristics in Table 3). The advantages of using emulsification procedures for ET AAS determinations rely on the higher sample throughput and improvement in the graphite tube lifetime as a result of using shorter furnace programs, thus leading to a significant reduction of the overall analysis cost [38]. Samples and standards, similarly prepared, can be placed directly in the autosampler cups and left open during measurement without fear of volatilization and loss of analytes. Such procedure cannot be applied in the direct injection mode because of the volatility and instability of samples and organometallic standards which must be used for calibration when the samples are only diluted in organic solvents [10]. Metals determination by ICP either OES or MS in emulsified samples also has important advantages like multielement analysis, reduction of matrix interferences, avoids overloading of plasma with organic solvents and allows the use of inorganic standards for calibration.

Triton X-100 was the surfactant most widely used for emulsions preparation from crude [38,39], fuel [40] and edible [41–43] oils, kerosene [48,49], gasoline [51–53], biodiesel [54] and naphtha [55,56]. Nonylphenol polyethylene glycol ether was preferred for crude [46] and lubricating [45,46] oils emulsification probably because its HLB is slightly higher than Triton X-100, which enabled higher solubility in water. Highly viscous samples like crude and fuel oils were first diluted with xylene [37–39] and toluene [40] respectively, compromising the limits of detection due to the increased organic load which may lead to the incomplete combustion of the organic matter [60].

Different inorganic acids like HF/HNO_3, HF/HCl or H_2SO_4 have been used for emulsion preparation [45–48], although nitric acid was preferred in most cases [49–56]. It is assumed that the acidic media both prevents hydrolysis of the metallic ions and also converts organic species, metallic solid particles and oxide species of the analytes into their inorganic forms. In addition, it has been demonstrated that the acidified samples in the emulsification process, enables direct correlation between the signal of the analyte in the samples and its signal in aqueous inorganic standards [61]. It was also found that nitric acid concentration has remarkable effect on the sensitivity of ET AAS and ICP measurements. Its reported optimum concentration varies in a broad range (0.2–10%), although in most procedures addition of concentrated acid to μL volumes of samples was reported. Whatever the acidic media used, the organic matrix is not destroyed; only elements extraction is carried-out [45,62].

Although manual mixing of the emulsion ingredients seemed to be successful and simpler to implement, ultrasound (US)-assisted emulsification allows obtaining stable and homogeneous emulsions more quickly in comparison with manual and mechanical processes (Table 3). However, some drawbacks related to the possible surfactant degradation can appear during US emulsification [63]. Then, detailed studies of the process must be performed when this approach is followed.

Also CVG combined with AAS, AFS or ICP is one of the most sensitive techniques available, but it is limited to a few analytes. Emulsification proved adequate to substitute the complete destruction of the organic matrix required in most cases. Therefore it was successfully applied to the determination of As, Cd and Hg in edible oils by ICP-MS [43], of MeHg and total Hg in fish-eggs oil [47] or biodiesel [71] by respectively introducing the analyte vapor into an AAS or AFS quartz cell. Total Hg was also determined in biodiesel by AAS after amalgamation on a Au–Pt net [54]. In all cases, the already prepared emulsion was automatically injected into the VG-AS system, as schematically shown in Fig. 1.

The heterogeneous nature of emulsions and the need for vigorous mixing of the ingredients greatly impair the on-line emulsification. There are only two reports devoted to on-line emulsion formation, both dedicated to multielement determination in edible oils by ICP OES/ET AAS [41] and ICP MS/FAAS [42]. A laboratory-made magnetic stirring micro-chamber and an ultrasonic probe were respectively incorporated into the flow manifolds for efficient mixing. When appropriately optimized, such systems are simpler, less time-consuming and less labor intensive than the conventional procedures. A simple diagram of such a system is shown in Fig. 2.

3.2. Spectrometric determination of chemical species using microemulsions

Microemulsions have also been extensively used in analytical chemistry to simplify the sample preparation procedures for the determination of metallic species in oily samples [10,57–59]. This section is dedicated to selected applications of microemulsions-mediated sample preparation for the determination of chemical elements in oils and fuels (Table 4).

Preparation of microemulsions in the presence of a surfactant and a co-surfactant, was found to be almost spontaneous and compatible to most spectrometric techniques readily used to quantify chemical elements in lubricating [32,33] and crude [34] oils, and in biodiesel [35,36]. To our knowledge, these are the only analytical applications where preparation procedures are in accordance with microemulsions definition.

Table 4
Trace elements determination in oils and fuels using microemulsion formation procedures.

Sample	Elements	Analytical technique	Sample processing (mixing type)	Calibration	Method validation	DL	RSD (%)	Ref.
Lubricating oils	Cr	FI-ETAAS	Sample + hexane + NaCl + SDS + sec-butanol. (Ultrasonic)	Aqueous standards in HNO_3	Certified materials	4 $\mu g\,L^{-1}$		[32]
Lubricating oils	Al	SI-ETAAS	Sample + surfactants mixture + sec-butanoln (Flow direction changes and ultrasonic)	Aqueous standards in HNO_3	Certified materials	2.3 $\mu g\,L^{-1}$	1.5	[33]
Crude oil	V, Ni, Pb	SI-ICP-MS	Sample + Triton X-100 + HNO_3 + tetraline (Manual)	Organometallic standards	Certified materials and standard addition	NR	1.5–2.9	[34]
Biodiesel and edible oils	Na, K	FAAS	Sample + HNO_3 + NaCl + Triton X-100 + pentan-1-ol (Manual)	Aqueous standards in high purity base mineral oil	European norm EN 14108 and EN 14109.	0.1 and 0.06 $\mu g\,g^{-1}$	0.4–1	[35]
Biodiesel	Cd, Co, Cu, Mn, Ni, Pb, Ti, Zn	ICP-MS	Sample + HNO_3 + Triton X-100 + propan-1-ol (Magnetic)	Aqueous standards in mineral oil	Recovery tests	$\mu g\,L^{-1}$ range	NR	[36]
Gasoline	Cu, Co, Pb	ETAAS	Sample + ethanol + HNO_3 + water (Manual)	Aqueous standards treated as samples	ETAAS after mineralization	2.5, 1.5, and 4.0 $ng\,g^{-1}$	NR	[64]
Gasoline	Pb	FAAS	Sample + propan-1-ol + water (Sonication)	Aqueous standards in Pb-free gasoline	Standard addition	0.07 $\mu g\,L^{-1}$	2.5	[65]
Gasoline	Cu, Fe, Pb, Ni	ETAAS	Sample + propan-1-ol + HNO_3 (Manual)	Aqueous standards in purified gasoline treated as samples	Comparative methods	0.4–3.0 $\mu g\,L^{-1}$	<5	[66]
Lubricating oils (W/O)	Ca, Mg, Zn	FAAS	Sample diluted in AVK + propan-1-ol + HNO_3 (Manual)	Aqueous standards in mineral oil treated as samples	FAAS after sample dilution in AVK and certified materials	0.17–4.3 $\mu g\,L^{-1}$	0.7–4.3	[67]
Edible oils, margarine and butter	Cd, Co, Cr, Cu, Ni, Mn	ICP-OES	Sample + propan-1-ol + HNO_3 + water. Fats first dissolved in xylene (Manual)	Aqueous standards treated as samples	Recovery tests and ETAAS after mineralization	$ng\,g^{-1}$ range	NR	[68]
Gasoline, diesel and naphtha	As	ETAAS	Sample + propan-1-ol + HNO_3 (Manual)	Aqueous standards	Independent procedures	1.2–1.8 $\mu g\,L^{-1}$	<5	[69]
Biodiesel and edible oils	As	ETAAS	Sample + propan-1-ol + HNO_3 (Manual)	Aqueous standards	Recovery tests with organic and inorganic species	0.3 $\mu g\,g^{-1}$	<5	[70]
Gasoline	Hg	CV-AAS	Sample + propan-1-ol + HNO_3 (Manual)	Aqueous standards	Recovery tests and CV-AAS after extraction	0.10 $\mu g\,L^{-1}$	5–8	[71]
Gasoline and diesel	Ni and Pb	ETAAS	Sample + propan-1-ol + HNO_3 (Manual)	Aqueous or organometallic standards in n-hexane	Independent comparative procedures	4.5 and 3.6 $\mu g\,L^{-1}$	1–4	[72]
Gasoline, diesel and naphtha	Mn	ETAAS	Sample + propan-1-ol + HNO_3 (Manual) Mechanical mixing before use	Aqueous standards in HNO_3	Standard method ASTM D 3831-90	0.6, 0.5 and 0.3 $\mu g\,L^{-1}$	6–8	[73]
Biodiesel	Na, K, Ca, Mg	FAAS	Sample + propan-1-ol + HNO_3 (Manual)	Organometallic standards.	Certified standard diluted in xylene	0.004–0.2 $\mu g\,L^{-1}$	<5	[74]
Naphtha	Cu, Fe, Pb, Si	ETAAS	Sample + propan-1-ol + HNO_3 (Manual)	Organometallic standards treated as samples	Direct ETAAS	0.01–26 $\mu g\,L^{-1}$	1.7–20	[75]
Diesel and asphaltene	V	ETAAS	Sample + propan-1-ol + HNO_3 Asphaltene was first dissolved in dichloromethane (Manual)	Aqueous standards. Treated as samples for asphaltene	Recovery test, Certified materials and ICP-MS	5 $\mu g\,L^{-1}$ and 4 $\mu g\,g^{-1}$	<8	[76]
Crude oil	Cd, Co, Cr, Fe, Mn, Mo, Ni, Ti, V, Zn	ICP-OES	Sample + propan-1-ol + HNO_3 + water (Ultrasonic)	Aqueous standards treated as samples	Certified materials and ICP-OES after mineralization	$ng\,g^{-1}$ range	0.9–2.7	[77]
Edible oils	Cu, Fe, Ni, Zn	HR-CS-FAAS	Sample + propan-1-ol + HCl (Manual)	Aqueous standards	ICP-OES after sample mineralization	0.12–0.62 $\mu g\,L^{-1}$	5–11	[78]
Gasoline	Cu, Fe, Pb, Zn	FS-FAAS	Sample + propan-1-ol + buffer followed by solid phase extraction (Manual)	Aqueous standards treated as samples	Recovery tests	3.1, 2.2, 2.3, and 2.6 $\mu g\,L^{-1}$	<10	[79]

DL, detection limit expressed as $\mu g\,L^{-1}$ or $\mu g\,g^{-1}$ for liquid or solid samples, respectively; NR, not reported; RSD, relative standard deviation; AVK, aviation kerosene; HR-CS-FAAS, high-resolution continuum source FAAS; SME-FAAS, sequential multielement FAAS; SI, sequential injection; FI, flow injection; SDS, sodium dodecyl sulfate.

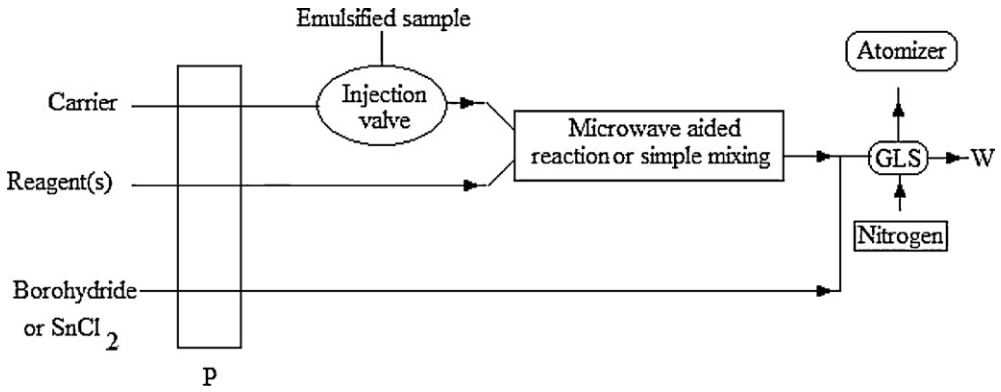

Fig. 1. Example of a flow injection CVG system for the determination of volatile species-forming elements in emulsified oily samples. According to application, the reagent(s) line could carry oxidizing or reducing agents, acids, etc. P, peristaltic pump; W, waste; GLC, gas liquid separator; CVG, chemical vapor generation; Atomizer could be AAS, AFS or ICP.

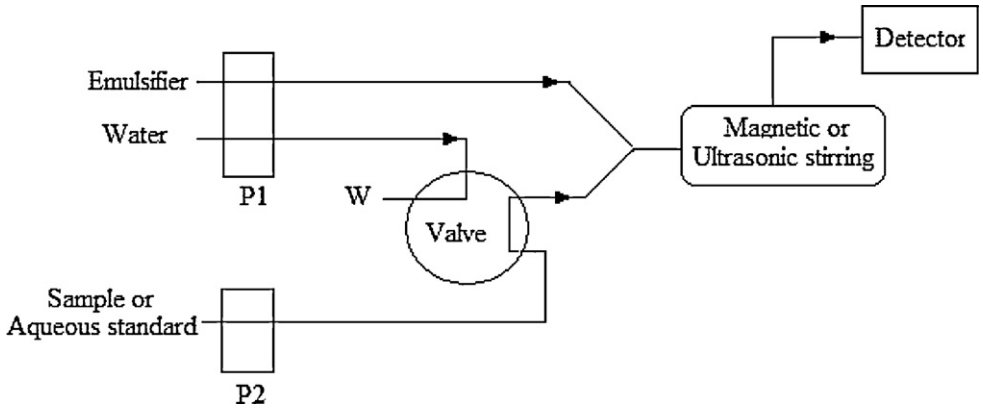

Fig. 2. Flow injection manifold for on-line emulsification of oily samples followed by AS detection. P1 and P2, peristaltic pumps; W, waste.

Burguera et al. described the determination of Cr [32] and Al [33] in lubricating oil by ET AAS after on-line emulsification using flow injection (FI) and sequential injection (SI), respectively. An example of the former is given in Fig. 3. The difference with the FI system resides in the fact that in FI the reagents are introduced through a peristaltic pump and ultrasonically mixed before selecting the desired segment to be introduced into the graphite tube. Off-line microemulsion preparation was also performed followed by SI [34] or in-batch [35,36] analytical measurements. Regardless their spontaneous formation, the adequate formulation of such systems required manual, mechanical or ultrasonic mixing (Table 4). Given the fact that the sample is kept homogeneously dispersed for a long period of time (some say indefinitely), added to the need to process a large number of samples in petroleum industries around the world, it is not understandable the lack of publications following such procedure.

During the last years, various Brazilian research groups have reported on the preparation of surfactant-free microemulsion systems. The simplest way was to stabilize samples like gasoline, lubricating oil or vegetable oils, margarine and batter with ethanol [64,66] or propanol [65–79] and water. Ozcan and Akman [64], and Cardarelli et al. [65] the only non Brazilians working with these systems, observed that microemulsions prepared from gasoline samples in ethanol were less stable than those prepared

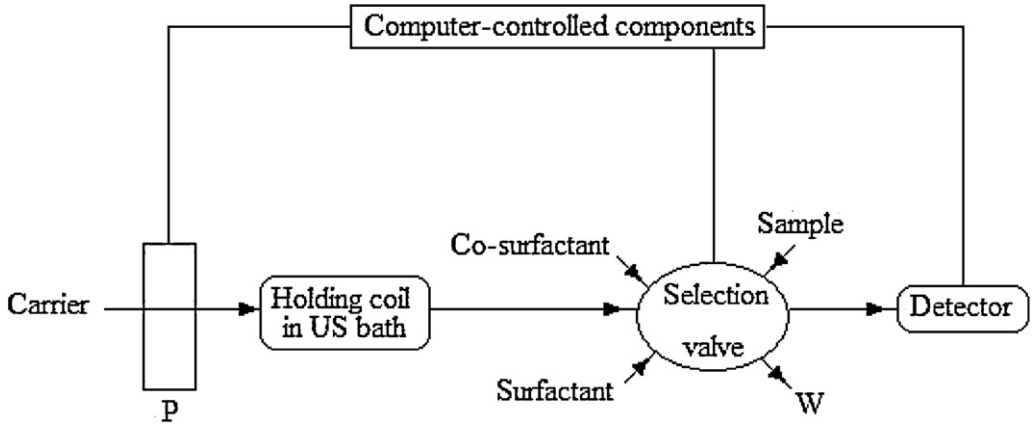

Fig. 3. Schematic diagram of a SI system for on-line microemulsion formation from oily samples. P, pump; US, ultra sonic; W, waste.

in propanol. This effect may be due to differences between the alcohols polarities. It means that propanol has a stronger interaction with the oil and aqueous phases of the microemulsion due to its lower polarity when compared to ethanol. However, most of the papers dealing with microemulsion preparation for AS metals determination report mixing all types of samples (crude, lubricating and edible oils, gasoline, diesel, naphtha, biodiesel and asphaltene) with co-surfactant (ethanol or propanol) and water [64–68], propanol and an aqueous solution of HNO_3 [69–77], HCl [78] or a buffer of pH 10 [79]. In most cases it is claimed that transparent, homogeneous and indefinitely stable solutions are obtained after gentle manual mixing. Without any reasonable experimental characterization, such preparations have been called three-component solutions [64–70], microemulsions [71–75,78,79], or detergentless microemulsions [76,77]. To avoid confusions due to the use of such nomenclature, unified criteria must be imposed. Furthermore, in order to get long-lasting, homogeneous and transparent solutions, the addition of the components must be made in a careful order [63]. The analytical publications seem not to pay much attention to this matter. Although not mentioned by the authors, a careful reading of the papers, reveal that the order of addition of the reagents to the sample has a relevant effect in the stability time of the final product: the stability reported varies from few minutes to several months or indefinitely.

It is assumed that detergent-free microemulsions tolerate higher amounts of sample, minimizing the dilution factor when compared to more traditional sample preparation procedures such as acid decomposition or emulsification using detergents. Aucelio and Curtius [80] recognized that better results were obtained when samples were introduced as microemulsions prepared with a surfactant compared to detergentless microemulsions at least for the determination of As, Sb and Se in gasoline and kerosene.

As shown in Table 4, certified reference materials (CRM) were used for method validation although in many cases no adequate material is available for the samples investigated. Therefore, the same analytical technique after sample mineralization was sometimes the choice to validate the procedure. So called independent procedures or standard methods were also applied to certify the accuracy of the proposed emulsification treatment of the samples. Some other times only recovery tests were performed by spiking the samples already prepared as microemulsions with adequate microvolumes of the working inorganic standards. This procedure is synonymous to the analyte addition technique which is trying to compensate for matrix effects. Beside the claims of 100% recovery, such experiments do not indicate the absence of systematic errors or that the proposed procedure has successfully been validated as the analyte is not added in the chemical form that it is present in the real samples and thus the agreement may only appear fortuitously [81].

4. Final comments

It is well documented that it is difficult to achieve accurate determination of trace elements in oils and fuels by AS techniques using their direct introduction into the analytical instruments because of the high instability of the signal. Metal losses from such samples during transport and storage require their stabilization immediately after sampling, particularly when $\mu g\,L^{-1}$ or $ng\,g^{-1}$ levels are to be determined. Furthermore, significant time is needed for sample treatment when conventional digestion procedures are used. Emulsification seems to solve many of these problems allowing a constant signal for the time needed to carry-on the analysis.

Proper understanding of the physical phenomena and the adequate formulation of emulsions and microemulsions is absolutely necessary in order to fully exploit the specific advantages of emulsification processes and their analytical applications. Although microemulsions are more stable than emulsions, in general, they require higher dilution of the samples due to the higher amount of surfactant needed for their formation. This fact leads to the development of procedures with poorer detection and quantification limits in relation to the formation of emulsions for the stabilization of samples. However, the concentration of elements found in commercial samples proved to be well above the detection limits of such a procedure.

As emulsions and microemulsions have similar viscosities with aqueous solutions, no problems were found with nebulization systems in FAAS and ICP-OES instruments, with signal instability due to sample evaporation from autosampler cups used in ET AAS determinations or with the CVG in FI systems. Also, matrix effects were not present when these assemblies are used. Conventional calibration can be made in all cases but the aqueous standards must be spiked into purified oils or other matching matrix treated in a similar way as samples.

Emulsions are strictly heterogeneous systems, but the spontaneous formation of homogeneous microemulsions offer the possibility of incorporating simple manifolds in automated systems connected to AS detectors for routine analysis. Most of these sample-preparation applications have been developed in discrete systems; nevertheless, as demonstrated by several authors, on-line approaches can be easily implemented, as the sample pretreatment step can be interfaced with others that are already automated like FI [32,41,42], SI [33,34] or CV-AAS [43,47,71] systems. The on-line emulsification is still not a procedure widely employed in the determination of metals in liquid oily samples by AS techniques. Unfortunately, the literature search does not show any recent activity in this matter. However, a considerable research effort is now in progress on the development of new pharmaceutical and cosmetic products which might need specialized analytical assistance. There is an obvious direct connection between the microstructure, the solubilization capacity, and the bioavailability of the active constituents in such products. Thus, it seems that future work will concentrate on the development of new and sophisticated analytical tools for the exploration of microemulsion microstructure; it is very important to know in which microstructure (W/O, bicontinuous, or O/W) the active molecules will be best accommodated, and also to find whether they are located in the core, between the surfactant hydrophobic tails, or close to the surfactant hydrophilic heads. The aggregate could be then engineered in such a way to be able to analyze only the concentrated structure. Furthermore, novel nanomaterials might be of analytical use in phase separation procedures for preconcentration or speciation purposes. Biodegradable nanoparticles are currently used in medicine to encapsulate different types of drugs to improve bioavailability, bioactivity and control delivery. The drug molecules are either entrapped inside or adsorbed on the surface [82]. Such procedures could be followed by analytical chemists and make them applicable to trace elements and/or their complexes determination. As another example, Qian and Zhang [83] reported the instant formation of an emulsion from a water-soluble porous polymer soaked in an oil phase. An imaginative analyst could design a simple FI manifold for the determination of traces of metals in oils using such materials.

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