Analytical Inorganic Extractions

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Historical Development

Trace elemental analysis is under constant development and the challenging analyses of today become the routine of tomorrow. Despite recent and rapid advances in analytical instrumentation, it is still necessary in many applications to use separation and preconcentration techniques prior to the analytical determination. Typically, the reason for performing a separation and/or preconcentration step is to bring the concentration of the trace element to a detectable level and/or separate it from interfering substances in the sample matrix. Separation and preconcentration are therefore a frequent component of an analytical scheme. Inorganic solvent extractions are also used extensively in industrial applications. Moreover a rapidly developing field, elemental speciation, will depend in part on sophisticated separation techniques such as liquid–liquid inorganic extractions.

Inorganic solvent extractions have been known and performed since the nineteenth century. The extraction of uranyl nitrate into diethyl ether was reported in the 1840s, but it was some time later before quantitative understanding of the inorganic liquid–liquid extraction distribution equilibria was forthcoming. Nernst presented the thermodynamical explanation of the distribution in the 1890s. Chelate extraction was also developing at this time, most notable was the use of 1,5-diphenylcarbohydrazide which chelated with chromium. The work of Fisher in the 1920s with dithizonates is noteworthy; this group studied the distribution of the elements as a function of reagent concentration, metal, complexing agents and pH. During this time, a wide array of solvent extraction methods was developed.

Rapid and distinguished progress in inorganic extractions occurred during World War II, most as part of the 'Manhattan Project' research in atomic energy. One of the most significant applications of liquid–liquid extraction in inorganic chemical technology was the separation of uranium and plutonium from nuclear reaction fission products in the late 1940s. Later, inorganic extractions replaced ion exchange at the beginning of the nuclear fuel cycle for separating uranium from other leach liquors.

Hydrometallurgical applications of liquid–liquid inorganic extractions are numerous and remain the contemporary choice of separation for many processes today. In addition, as environmental regulations develop, increased interest in recovery methods for metals from a variety of waste streams will no doubt renew interest in metal separation techniques.

The prevailing industrial use of inorganic solvent extraction includes the separation of the lanthanide (III) ions. Individual lanthanides are widely used in many of today's 'high-technology' applications for example, lasers (neodymium in yttrium–aluminum garnet), superconducting materials, specialty ceramics, catalyst, the nuclear industry and colour video phosphors.

Inorganic Processes

Solvent extraction, ion exchange, volatilization and precipitation are the most commonly used separation approaches for trace elemental analysis. Inorganic preparation schemes generally follow a flow diagram, as shown in **Figure 1**.

The processes by which extraction of inorganic compounds occur using organic solvents are varied and may be relatively involved. Consequently, attempts to classify inorganic extraction processes are difficult. Attempts have been made, based on the identity of the extracted compound, or of the extracting agent, or pH of the extraction solution. For the purposes of this chapter, a simple subdivision will be adopted based on the extraction reagent used.

Extraction Considerations

The need for separation and/or preconcentration in trace metal analyses are fundamentally related to available instrumentation and instrumental

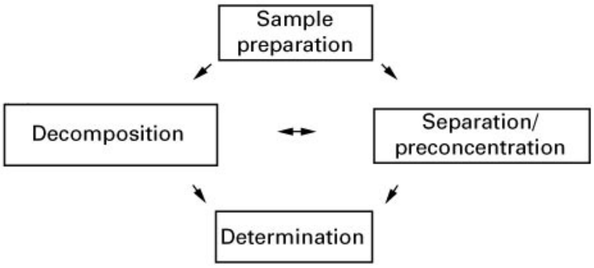


Figure 1 Inorganic preparation flow diagram.

Table 1 Comparison of a select list of analytical techniques[a]

Comparison	*ASV*	*Flame AAS*	*ET-AAS*	*ICP-AES*	*NAA*	*ICP-MS*
General detection limits	0.1–0.01 mg L^{-1} (ppb)	1–5000 mg L^{-1} (ppb)	0.1–0.001 mg L^{-1} (ppb)	1–100 mg L^{-1} (ppb)	1–1000 mg L^{-1} (ppb)	0.01–1 mg L^{-1} (ppb)
General sensitivity	Excellent, select elements	Moderate, refractories poor	Excellent, refractories limited	Moderate, refractories excellent	Moderate	Excellent
Instrument maturity	Well established	Well established	Well established	Established and growing	Established	New and growing
Interferences	Some	Few, well understood	Many, controllable	Spectral	Few	Moderate, mass overlap
Instrument availability	Readily	Readily	Readily	Readily	Specialized laboratory	Specialized laboratory
Instrument-specific inorganic extraction	Developed	Numerous, well developed	Well developed	Developed	Well developed	Undeveloped

[a]Abbrevations: ASV, anodic stripping voltametry; Flame AAS, flame atomic absorption spectrometry; ET-AAS electrothermal atomic absorption spectrometry; ICP-AES, inductively coupled plasma atomic emission spectrometry; NAA, neutron activation analysis; ICP-MS: inductively coupled plasma mass spectrometry.

capabilities. Basically, separation and/or preconcentration are needed when one of the following situations occurs: concentration of analyte is below the sensitivity of the instrumental method; interferences exist in the sample (relative to the instrument to be used); or physical or chemical states of the sample are not appropriate for the instrument. Sensitivities for elements varies with the instrumental method and are relative to matrix type; however, a general listing of sensitivities of commonly used analytical equipment is given in **Table 1**.

The impetus for doing an extraction will therefore depend on the availability of instruments and the capability of the instrument relative to the matrix type (i.e. interferences). Inorganic extraction schemes are typically instrument specific. Although instrument development has significantly reduced detection limits, availability of some of the more state-of-the-art equipment is still limited to specialized or well-equipped laboratories. The need for separation and preconcentration therefore still exist. Speciation studies will also continue to support development and research into inorganic separations from complex matrices.

Because atomic absorption spectrometry (AAS) is readily available, but the detection limits are high in relation to today's needs, there are numerous solvent extraction methods available for metals in AAS analysis. Several excellent sources are listed in Further Reading; these have lengthy tables of inorganic extraction schemes.

Theory and Equations of Inorganic Solvent Extraction

The solvent extraction process to separate and/or preconcentrate an analyte of interest is performed by using two immiscible solvents. A complex (typically neutral in charge) is formed with the element of interest, typically in an aqueous solution and will partition into a mutually insoluble (organic solvent) phase. The Nernst partition (or distribution law) states that at equilibrium a given solute will be distributed between two essentially immiscible liquids according to the following equation:

$$K_D = \gamma_o[A]_o/\gamma_{aq}[A]_{aq}$$

where K_D is the distribution coefficient (also called the partition coefficient) and $[A]$ is the concentration of the analyte, γ are activity coefficients, subscript 'o' denotes organic phase and the 'aq' subscript denotes aqueous phase. The above equation holds true in only the most rigorously well-defined thermodynamic systems. For simplicity the relationship assumes that no side reactions occur in either the aqueous or organic phase and that no stable intermediates are formed with the analyte (e.g. metal) of interest. From a practitioner's standpoint, the total amount of analyte (e.g. metal) transferred from one phase to the other is of most interest. An empirical distribution ratio, D, is defined by the simplified relationship given below:

$$D = [A_T]_o/[A_T]_{aq}$$

where $[A_T]_o$ includes all (T = total) complexes of the analyte of interest in the organic phase and activity coefficients are assumed unity. The assumption of $\gamma = 1$ for chelating extractions is reasonable. However, for ion-pair extractions where the electrolyte concentration is high, to assume unity for the activity coefficients is a poor assumption. The simplifying relationship is still often employed, however, with the assumption that the (γ_o/γ_{aq}) ratio will remain constant.

The extraction efficiency, $\%E$, which defines the amount of analyte transferred from the aqueous phase to the organic phase, is defined as follows:

$$\%\ \text{Extraction} = 100D/\{D + (V_{aq}/V_o)\}$$

where V_{aq} is the volume of the aqueous phase and V_o is the volume of the organic phase. An important property of the above relationship is that the extraction efficiency is independent of the initial analyte concentration. High extraction efficiencies can be achieved when the V_{aq}/V_o ratio is small (that is, small aqueous volumes used with large organic volumes). There is of course a practical limit to this approach. Multiple extractions with reasonable volumes perform better than a single extraction with one large volume. Large values of D, distribution ratio, correspond to high extraction efficiencies (e.g. $D = 100$ then $\%E = 99\%$, $D = 0.1$ then $\%E = 10\%$, for a 1 : 1 volume ratio).

An extraction reaction may be described by the general chemical equation given below:

$$A^{n+}_{aq} + n\text{HX} \leftrightarrow A\text{X}_{no} + n\text{H}^+$$

where A is the analyte of interest (e.g. metal ion) with charge n^+, HX is the extracting agent (e.g. chelating agent). Note, that extracting agents are often acidic. From the following extraction reaction the equilibrium constant, K_{ex} is:

$$K_{ex} = [A\text{X}_n]_o[\text{H}^+]^n/[A^n]_{aq}[\text{HX}]^{n_o}$$

By substituting the distribution ratio, D, the equation simplifies to:

$$K_{ex} = D\{[\text{H}^+]^n/[\text{HX}]^n_o\}$$

hence:

$$D = K_{ex}[\text{HX}]^n_o/[\text{H}^+]^n$$

The logarithmic form for the distribution coefficient is then:

$$\log D = \log K_{ex} + n\text{pH} + n\log[\text{HX}]_o$$

From this model, for a given system, the degree of extraction increases as the concentration of the chelate $[\text{HX}]_o$ increases. Extraction increases with increasing pH (decreasing hydrogen concentration) in the aqueous phase. A one unit increase in pH results in a factor of 10 increase in the distribution coefficient for $n = 1$; for $n = 2$, the distribution coefficient increases by a factor of 100. Hydrolysis of the metal ion and decreased solubility of the chelate occur at high pH limiting this general approach.

Plots of $\log D$ versus pH (or $\%E$ versus pH or versus $\text{pH}_{1/2}$) are often used to define extraction systems. These types of plots produce sigmoidal curves, with the overall position relative to the pH axis dependent on K_{ex} with the slope $= n$. For purposes of comparison, if $D = 1$ (i.e. $E = 50\%$) and $[\text{HX}]_o = 1$, the pH is constant and equal to $\log K_{ex}/n$. This term is referred to as $\text{pH}_{1/2}$, and is characteristic of the extraction process. Analyte/chelate agent values of $\text{pH}_{1/2}$ are often cited and are used as a measure of the feasibility of separating two analytes.

Further theoretical discussion is beyond the scope of this chapter but includes topics on solvent properties, such as the solvent Hildebrand parameter, solvent dielectric constant, and complex properties such as the complex size, polarity and polarizability, as well as pH, temperature and reaction kinetics.

Inorganic Solvent Extractions

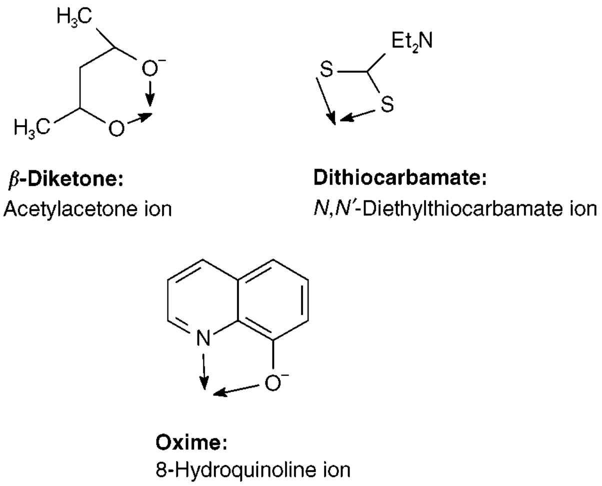
The essential prerequisite for an element to be extracted from an aqueous solution is that it be part of a neutral complex. Charge neutrality reduces the electrostatic interactions between the element (analyte of interest) complex and water and therefore lowers the solubility of the complex in water. Consequently, the neutral complex can be extracted into the less polar organic solvent. General attributes and chemical properties that can facilitate separation are: charge neutrality, increase size of complex formed and incorporation of hydrophobic or organophillic properties. These general attributes can be accomplished by several mechanisms including the element associated with naturally occurring complexants, chelate complexes formed with analyte and ion-associated (ion-paired) complexes. All three mechanisms can and will form a neutral complex with the analyte of interest. Depending on the ligands (complex associated with the element) other chemical properties such as complex size and hydrophobic/organophillic properties can be incorporated.

Extraction Schemes

Classification schemes are numerous and no one scheme covers all systems. The most common schemes are based on the form of the extracted element that transfers into the organic phase. This simplified classification scheme is adequate for the discussion here. However, even with simple schemes the categories are not exclusive, and some extraction agents could be classified into other categories. The experimental process of inorganic extraction of a neutral complex, regardless of the type of complex, is essentially the same. The neutral complex's interaction with the aqueous phase, including but not limited to the solubility, depends on the charge and polarity of the overall complex. The first step is to generate a neutral complex with the analyte of interest through one of the mechanisms listed above. A small volume of organic solvent is added to the sample mixture. For example, a 1 L aqueous sample may be extracted into 40 mL of organic solvent. Extraction can be performed in a separatory funnel or by using a mechanical shaker table. The pH of the mixture may need to be manipulated, depending on the exact extraction scheme used. In addition, masking agents may be used to obtain specificity (see below). After mixing, the two phases are separated and the procedure is generally repeated several times. The organic phase is combined from each extraction. The concentration of the elements in the sample is increased by 1–3 orders of magnitude in the organic phase. The extract can then be further pre-concentrated if needed (back-extraction, evaporation, etc.) or analysed directly, for example by flame AAS.

Naturally occurring complexants Elements that can form neutral complexes can already exist in naturally occurring water systems. These complexes are formed essentially with covalent bonding between the element and naturally occurring ligand(s). Ligands are molecules or ions bonded to a central metal ion and tend to be Lewis bases; also included in this category would be undissociated covalent species. Examples of this category would include I_2 and B_2, the halides of some metals ($GeCl_4$ $HgCl_2$, $AsCl_3$) and oxides of some metals (OsO_4). The extraction of these types of compounds would proceed in the same manner as for chelates and ion-associated complexes.

Chelates A chelate is a type of ligand. A multidentate (*dentate* is Latin for tooth) ligand that uses more than one atom to bind to a metal in a coordination complex, see **Figure 2**. The metal is the electron-pair acceptor and the chelating agent the electron-pair donor. When binding to the metal ion, the chelate (ligand) forms a ring of atoms, of which the metal is one member. The chelate complex charge exactly neutralizes the charge on the metal ion. Most rings contain > 4 and < 8 atom members; the most stable typically is a 5-membered ring. Bidendate describes a chelate where two atoms from the chelate complex bond to the metal and tridentate would indicate three coordinating atoms. Many chelating extractants are weak acids, therefore, control of pH is important in many extracting schemes.



β-Diketone: Acetylacetone ion

Dithiocarbamate: *N,N′*-Diethylthiocarbamate ion

Oxime: 8-Hydroquinoline ion

Figure 2 Chemical structures of typical chelate–metal complexes.

An exhaustive treatment of every chelate system is beyond the scope of this chapter. **Table 2** lists a selection of chelate types with one or two specific chelate agents listed below these. To describe the selectivity of each is not possible in a brief chapter, a sense of the ability of each chelate reagent is given by listing the wide range of complex-forming metals that are possible. Detailed information about the selectivity, solvent and other experimental conditions can be found in the references listed in Further Reading. The list in Table 2 include inorganic extraction procedures for a wide array of instrumental methods including: flame AAS, electrothermal (ET)-AAS, inductively coupled plasma-atomic emission spectroscopy, (ICP-AES), neutron activation analysis (NAA), spectrophotometric, chromatographic, flame photometry, and polarography. In addition, most of the chelate groups listed in Table 2 are compatible with more than one organic solvent. Solvent flexibility in an analytical scheme allows an extended range of instrumental methods which can be used for the determination.

Inorganic extraction, utilizing chelates, for analytical separation and/or preconcentration has been exploited for many instrumental systems. For flame AAS analysis, often the inorganic solvent extraction is designed to increase the concentration of elements of interest and, most importantly, reduce the concentration of alkali and alkaline earth elements (i.e. leave most of them in the aqueous phase). This separation

Table 2 A select list of inorganic extraction systems

	Metals extracted
Chelating agents	
Oxines	
-8-Hydroxyquinoline -(and derivatives)	> 50 metals
α-Dioximes	
-Dimethylglyoxime	Ni, Pd, Co
Dithizones	
-Diphenyldithiocarbazone	> 30 metals
Dithiocarbamates	
-sodium diethyldithiocarbamate	> 50 metals
-Sodium *N′N′*-phenylacetyldithiocarbamate	> 50 metals
β-Diketones	
-Acetylacetone	> 50 metals
-Thenoyltrifluoroacetone	> 50 metals
Nitrosoarylhydroxylamines	
-Ammonium *N*-Nitroso-*N*-phenylthydroxylamine (cupferron)	> 30 metals
Organophosphorus acids	
-di-*n*-butylphosphoric acid	> 30 metals
-Di(2-ethylhexyl)phosphoric acid	> 30 metals
1-Nitroso-2-naphthol	Co(II)
1-(2-Pyridylzao)-2-naphthol (PAN)	> 50 metals
Ion-pair agents	
Chelated ion-pairs	
-ethylenediaminetetraacetic acid (EDTA)/halide	> 30 metals
-1,10-phenoanthroline/perchlorate	Fe (II)
Non-chelated ion-pairs	
-tetraalkylammonium salts	> 50 metals
-tetraphenylarsonium salts	> 50 metals
Halide ion pairs	
-HCl	> 50 metals
-HF	> 50 metals
-HI	> 50 metals

is especially necessary for many natural water samples such as seawater, brines, etc. Trace element analyses of clinical samples such as blood, urine, etc., also benefit from inorganic extraction for flame AAS analysis as well as other determination techniques (ET-AAS, ICP-AES, etc.). Radiochemistry separations for NAA also often use inorganic extraction techniques that utilize chelating schemes.

Extraction schemes have also been developed which leave the analyte of interest in the aqueous phase and remove interferences through the organic phase. This technique has limited applicability owing to the limited solubility of the (starting reagent) chelate in organic solvents.

Ion association (ion pair) Neutral complexes can be formed through ion association (ion-pair) and extracted from an aqueous solution into an organic solvent. Ion association inorganic extracts encompass a wide range of extraction schemes. General sub-groupings include chelated ion pairs, nonchelated ion pairs and halide–cation ion-pairs. The halide–cation pairs are typically extracted into oxygen-containing solvents, such as methyl isobutyl ketone, diethyl ether and alcohols. A select list of ion pair extracting agents is given in Table 2.

Maximizing the coulombic forces of attraction between the ion pairs facilitates extraction of the ion pairs. The dielectric constant of the solvent is a large contributor to the overall extractability of a scheme. Enhancement of the extraction of ion-associated complexes is increased by the addition of electrolytes, called ‘salting-out’. The salting-out effect may be attributed to the increase in anion concentration, as well as the decrease of the dielectric constant of the aqueous phase. Complexes can be formed by ligands coordinated to the metal and an appropriate counter anion that neutralizes the total charge. One of the ions (either the complexed ligand or the anion) typically contains a large hydrophobic group(s) which further enhances extraction of the ion pair into the organic phase.

Factors Affecting Inorganic Solvent Extractions

Control of pH is critical to ensure conditions are favourable for the formation of the desired complexes. The extraction specificity needed influences the acceptable range of pH. Many inorganic extraction schemes use buffers. The lack of a buffer in an inorganic extraction should be viewed with suspicion, since the quantity of metal extracted is strongly pH dependent. In addition, chelating agents will alter the pH of the solution. Several buffers have been used for inorganic extractions for AAS determination, including borate, phosphate, citrate, acetate and formate. Acetate should not be used if lead or silver or other stable metal acetates are to be determined. Buffers can be a significant source of contamination, as can any unpurified reagent added to a sample.

The nature of the solvent is of special importance for inorganic extractions. There are several criteria which should be evaluated when choosing a solvent for an inorganic extraction. The solvent should have the following characteristics:

- Extracts the desired metal chelates
- Immiscible with aqueous solution (i.e. low solubility in water); for convenience, density > water if the sample is drawn off
- Does not form emulsions

- Compatible with the analytical determination technique
- Environmentally safe and nontoxic
- Available in an acceptably uncontaminated state.

In the case of flame AAS, ketones or esters are commonly used extraction solvents. The list of organic solvents used in inorganic extractions is extensive.

Masking Agents

When the desired specificity for separation cannot be controlled sufficiently by pH modification, addition of a masking agent will frequently be used. Masking agents are complexing agents that form water-soluble complexes which then compete with the extracting agent. The masking agents prevent the extraction of the metals they react with, by forming water-soluble complexes (strong polar complexes) which remain in the aqueous phase. Some extracting agents are specific and many others can be made specific using pH control and/or a masking agent. The most commonly used masking agents include cyanide, thiocyanate, thiosulfate, tartrate, carbonate, citrate, fluoride, bromide, iodide and ethylenediaminetetraacetic acid (EDTA). The effectiveness of masking agents is pH specific, ranging from acidic to basic conditions. In some schemes, more than one masking agent may be used.

Applications

Inorganic extractions are used in both analytical and industrial fields. Chelates form an important part of inorganic extractions and have extensive application in many areas of science and industry.

As discussed above, analytical applications include the separation and/or preconcentration of an analyte for determination. Another analytical application is the use of inorganic extraction techniques for reagent purification by removing trace metals (e.g. purification of aqueous buffers). Extraction of metals into nonpolar organic phases crosses many scientific disciplines. For example, crown ethers are used extensively as phase transfer catalysts. Crown ethers extract an element (e.g. K^+) from the aqueous phase into an organic phase. The K^+ ion is engulfed (chelated) in the centre of the crown ether. A class of antibiotics, the ionophores (e.g. nonactin, valinomycin, gramicidin, etc.) work much like crown ethers: they alter the permeability (distribution) of bacterial cells to metal ions and thereby disrupt their metabolism.

An example of a large-scale inorganic metallurgical extraction, is the Purex process used to extract uranium isotopes and plutonium. Once the uranium ore (e.g. carnotite) is crushed, it is concentrated by physical means; the uranium is then further concentrated by flotation methods. The ore is then roasted and leached with sulfuric acid (often with an oxidizing agent) and precipitates as sodium diuranate, a bright yellow solid called 'yellowcake'. This solid dissolves in nitric acid producing uranyl nitrate. The inorganic solvent extraction (Purex process) extracts the uranyl nitrate from the aqueous solution into tributyl phosphate in an inert hydrocarbon diluent: the impurities remain in the aqueous phase.

The aim of speciation studies is to identify and quantify all species that together combine to comprise the total element concentration. This is typically achieved by physicochemical techniques. A range of physicochemical separation techniques has been applied to speciation studies, including inorganic solvent extraction.

Inorganic chelate extractions are used extensively in industrial applications. A brief listing includes the following applications:

- Metallurgical extraction
- The chelate: (EDTA)
  - used in water softeners
  - boiler scale removal
  - industrial cleaning
  - soil metal micronutrient transport
  - food preservation
- The chelate: nitrilotriacetic acid (NTA)
  - similar applications to those listed for EDTA
- Ion exchange resins can be chelates
  - water purification processes
- Zeolites are a type of chelating ion exchange resin
  - water purification processes

Future Developments

Although instrument development has had a significant impact on inorganic extractions and the direction of research on separation and preconcentration techniques, there remains an extensive need and interest in inorganic solvent extraction techniques. One area which is currently under intense investigation is speciation. Chemical–physical methods of separation incorporating inorganic extractions remain an important part of this field. Another area of development is the recovery and removal of metals from industrial waste streams.

See also: **II / Chromatography: Liquid:** Ion Pair Liquid Chromatography. **Ion Exchange:** Theory of Ion Exchange. **III / Ion Analysis:** Liquid Chromatography.

Further Reading

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Extraction With Supercritical Fluid

See **II / EXTRACTION / Supercritical Fluid Extraction**

Inorganic Extractions

See **II / EXTRACTION / Analytical Inorganic Extractions**

Microwave-Assisted Extraction

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Introduction

Common extraction techniques for solid matrices include Soxhlet extraction, sonication extraction, supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), and accelerated-solvent extraction (ASE).

Soxhlet extraction allows use of large amount of sample (e.g. 10–30 g), no filtration is required after the extraction, the technique is not matrix dependent, and many Soxhlet extractors can be set up to perform in unattended operation. The most significant drawbacks of Soxhlet extraction are: long extraction times (e.g. up to 24–48 h), large amount of solvent usage (300–500 mL per sample), and the need for evaporation after sample extraction.

Sonication extraction is faster than Soxhlet extraction (30–60 min per sample) and allows extraction of large amount of sample with a relatively low cost, but it still uses about as much solvent as Soxhlet extraction, is labour intensive, and filtration is required after extraction.

The newer extraction techniques such as SFE, MAE, and ASE are very attractive because they are a lot faster, use much smaller amounts of solvents, and are environmentally friendly techniques. For example, SFE uses carbon dioxide or modified carbon dioxide (e.g., carbon dioxide containing a small amount of an organic solvent known as modifier) for extraction. Carbon dioxide is a nontoxic, nonflammable, and environmentally friendly solvent. Furthermore, the extraction selectivity can be controlled by varying the pressure and temperature of the supercritical fluid and by the addition of modifiers.

MAE uses microwaves that can easily penetrate into the sample pores causing the solvent trapped in the pores to heat evenly and rapidly. In contrast to conventional heating where it takes a long time for the vessel to heat and then transfer its energy to the