Additional material for Chapter 3 (to section 3.6.2 and examples given) and to aid Activity 3.4: Solvent Extraction of analytes.

Solvent Extraction

We have noted that in quite a number of cases, we are required to "extract" our analyte of interest from a solid sample. When released from the solid sample's matrix, this process must be both efficient (→ 100% of analyte extracted) and must maintain the integrity of the analyte, in the form required for its measurement. If this analytical measurement is based upon the identity of an element only, independent of its bound environment, then this is not so problematic and release of the analyte may even extend to a digestion process being undertaken (see Figure 3.3 in chapter 3 of the book). A problem can arise when the analyte's integrity is based upon, say, a molecular species or the oxidation state of an 'element ion', etc. that must be maintained. Therefore, we can see that if there is a requirement for the analyte to remain unchanged, it will need to be effectively "dissolved" out from the matrix. A suitable approach to this extraction problem is to consider acquiring our unchanged analyte through its efficient solubility in a "chosen solvent"; but one which is also 'compatible' with the solid matrix. The latter considers the "chosen solvent's" ability to both 'wet' and to 'permeate' the solid matrix and therefore release the analyte in the required form. If this efficient target dissolution of the analyte is possible without dissolving part of the matrix itself (which may complicate, or even interfere in, the later analytical measurement) then, all the better.

After defining the types of sample and analyte (Chapter 3, figure 3.1), this should provide us with a greater understanding of what we are dealing with, in preparation for the requirements of the later measurement step. If, after considering the flow chart figure 3.3, we come to the stage where we require a suitable solvent to "extract" the analyte of interest then the following points may be considered:

i) Is the **solubility** of the identified analyte (unchanged) **in the "chosen solvent"** suitably high? – check in validated sources
ii) Is the "**chosen solvent**" able **to 'wet' and to permeate the matrix** of the sample and therefore release efficiently, the contained analyte of interest? – check using validated sources
iii) What are the **conditions** required **to maintain integrity of the analyte** and efficiently extract the analyte of interest? – check using validated sources

This decision process would obviously be helped by information originating from validated sources which have already identified the measurement of that particular analyte, extracted from the given sample matrix using a chosen solvent; such validated sources include those found in standard official methodology texts (e.g. AOAC, USDA, FDA, ISO, FSA, EA and EPA methods; public analysts methodology; peer-assessed validated analytical papers etc.). Some examples of EPA extraction methods with given solvent systems are identified at the end of this overall section on "solvent extraction" (see below).

These methods, while tried and tested, are usually the result of certain approaches taken because of the underlying chemical and physical properties of the analyte, the solvent and the sample matrix. It has been noted in the book that one 'rule of thumb' to be considered when it comes to solvent selection is that: "like, dissolves like". This selection process often includes considering properties such as the 'polarity' of the analyte and the solvent together with that of the matrix.

Various examples of the extraction of analytes from given sample types / matrices, are shown throughout the book but the following stepped process may be considered a guide, especially when a completely different and new sample / analyte system may have to be considered.

Is the analyte ionic and inorganic in nature? e.g. NO_3^- **;** element ion such as Na^+; molecular or elemental; charged species; oxidation state

Is the analyte polar and inorganic in nature? e.g. $\mathbf{NH_3}$; PCl_3 ; molecular, heteronuclear and neutral

Is the analyte non-polar and inorganic in nature? e. g. $\mathbf{S_8}$; $\mathbf{P_4}$; Cl_2 ; I_2 ; O_2 ; elemental and non-metallic and neutral

Is the analyte ionic and organic in nature? e.g. CH_3COO^- acetate ion; $(CH_3)_3$-As^+-CH_2-COO^- Arsenobetaine; molecular and carbon-based

Is the analyte polar and organic in nature? e.g. $(CH3)_{\mathbf{2}}$-C=O propanone; CH_3-CH_2-CO-NH_2 propanamide; carbon-based with heteronuclear-based functional groups and neutral

Is the analyte <u>essentially</u> non-polar and organic in nature? e.g. $C_6H_5CH_3$ toluene; $\mathbf{CH_3\text{-}(CH_2)_{16}}$-COOH stearic acid; mainly carbon-based and possibly with only a small neutral heteronuclear contribution to the overall organic (hydrocarbon) structure.

The above steps allow identification of the character of the analyte to be measured; from ionic through polar to non-polar, for both inorganic and organic species.

A similar appraisal of the character of the sample matrix should be undertaken, in order to estimate the compatibility of any chosen solvent system in the extraction process.

To illustrate the importance of the latter step, imagine that you wish to extract a water soluble analyte (e.g. Na^+) directly from the insides of a freshly acquired sample of pine needles **without** destroying the sample matrix (which is needed for further analyses). Using the characterisation steps above we see that for the analyte we are dealing with a simple ionic elemental system. Therefore, a simple aqueous (water-based) extraction in theory would be, 'all that is needed' for the highly water soluble Na^+ analyte, even if present as salt crystals: NaCl – wouldn't it?

However, as we know, a waxy coating exists over the fresh pine needles which make-up the sample, rendering the surface of the sample matrix "hydrophobic". This 'epicuticular wax' coating, is essentially an organic, non-polar aliphatic hydrocarbon with limited functional

groups present. It is there to help reduce water-loss from the plant's thousands of leaf-like needles. A simple water only solvent (polar) will not 'wet' and permeate the sample's matrix coating (non-polar) in order to efficiently extract the analyte of interest (Na^+; mainly ionic-like if present in salt form, Na^+Cl^- or possibly very highly polar if associated with organic functional groups such as 'carboxylic acid'). A **solvent system** is required that both wets and permeates the sample while still being able to "dissolve" (solvent extract) the analyte of interest.

While water itself is a polar solvent that can support certain ionic and highly polar covalent analytes in solution, both water and a 'suitable' miscible organic solvent in admixture would present the necessary solvent properties for a selected extraction and also the wetting / permeation process. Obviously the other solvent will affect the solubility of the Na^+ in the water fraction of the solvent system but that miscible solvent chosen to accompany the water should still allow efficient extraction. One **solvent** that can be **used to mix with water**, still allows **some solubility of Na^+** and other highly polar Na-containing species, and possesses the necessary **wetting characteristics for a low to non-polar matrix**, is 'Ethanol'.
The Table shown below demonstrates both the type and progression of solvent polarity for a range of liquids that can be used in a solvent extraction process.
The table may also be used as a guide for selection of a suitable solvent for both solvent extraction from solid matrices and in liquid-liquid extractions (see Separations Table 3.7 and Solvent Extraction Methods Table 3.8 in Chapter 3 of the book). A 'miscibility' table is therefore of importance where two or more solvents are required to be compatible (miscible) or where they are required to be immiscible (incompatible and separate) for liquid-liquid extraction purposes. The table below includes the 'level of miscibility' of solvents with water, to further illustrate the point. However, a full 'miscibility' table for most solvents can easily be found on-line and in many books.

When an organic system is solely being considered as the solvent, then one or more (a combination) in the following list may be of interest:

Solvent	Formula	Polarity Index ‡	Polarity Index*	Solubility with Water (g/100g H_2O)	Boiling Point / ^oC	Dielectric Constant	Dipole Moment (D)
Pentane	$CH_3CH_2CH_2CH_2CH_3$	0.0	0.09	0.04	36.1	1.84	0.0
Cyclopentane	C_5H_{10}	0.1	(0.1)	0.016	49.3	1.97	0.0
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	0.1	0.09	0.01	68.7	1.88	0.0(8)
Cyclohexane	C_6H_{12}	0.2	0.06	0.005(5)	80.7	2.02	0.0
Carbon Tetrachloride	CCl_4	1.7	0.52	0.08	76.7	2.24	0
Toluene	$C_6H_5CH_3$	2.4	0.99	0.052	110.6	2.38	0.31

O-Xylene	$C_6H_4(CH_3)_2$	2.5	(0.74)	0.02	144.4	2.57	0.45 (→0.64)
Diethylether	$CH_3CH_2OCH_2CH_3$	2.8	1.17	6.1	34.5	4.3	1.15
Cyclo-hexanone	$C_5H_{10}C{=}O$	2.8	2.81	2.3	156	18.2	3.1
Dichloro-methane	CH_2Cl_2	3.1	3.09	2	39.7	8.93 (9.08)	1.6 (1.14)
Iso-propyl alcohol	CH_3-CH(-OH)-CH_3	3.9	5.46	Miscible	82.3	18.3 (19.92)	1.66
Ethyl Alcohol	CH_3CH_2OH	(4.0)	6.54	Miscible	78.3	24.55	1.69
Tetrahydrofuran	C_4H_8O	4.0	2.07	30	66	7.58	1.75
Chloroform	$CHCl_3$	4.1	2.59	0.795	61.1	4.81	1.15
Methyl-isobutyl Ketone (MIBK)	$(CH_3)_2CHCH_2COCH_3$	4.2	2.69	1.91	117 - 118	13.11	2.8
Ethyl Acetate	CH_3-C(=O)-O-CH_2-CH_3	4.4	2.28	8.7	77.1	6.02	1.88 (1.78)
Ethyl Methyl Ketone (Butanone)	$CH_3C(O)CH_2CH_3$	4.7	3.27	27.5 (25.6)	79.6	18.51	2.76
1,4-Dioxane	$C_4H_8O_2$	4.8	1.64	Miscible	101.1	2.25	0.45
Cyclohexanol	C_6H_{11}-OH	5.0	5.09	4.3	161	15.0	1.8
n-Octanol	$CH_3(CH_2)_6CH_2OH$	5.43	5.37	0.6	194	10.3 (3.4)	1.9
Acetone (Propanone)	$CH_3C{=}OCH_3$	5.1 - 5.4	3.55	Miscible	56.3	20.7	2.69
Methanol	CH_3OH	5.1 – 6.6	7.62	Miscible	64.7	32.70	2.87
Acetonitrile (Ethano-nitrile)	CH_3CN	5.8	4.60	Miscible	81.6	37.5 (38.8)	3.44 (3.92)
Acetic Acid	CH_3COOH	6.2	6.48	Miscible	118	6.2	1.7
N,N-Dimethyl Formamide (DMF)	H-C(=O)$N(CH_3)_2$	6.4	3.86	Miscible	153	36.71 (38.25)	3.86
Nitro-methane	CH_3-NO_2	6.8	4.81	9.5	101.2	35.9	3.56
Dimethyl Sulfoxide (DMSO)	CH_3-S(=O)-CH_3	7.2	4.44	25.3	189	46.68	4.1
Water	H_2O	10.2	10.0	Miscible	100	78.54 (80.1)	1.87

‡ Solvent Polarity Index is an empirical scale. Different scales are available, based upon different physico-chemical parameters and the scale shown in this column is one of the more common progressions – from ‘0’ (non-polar) to water set to ’10.2’.

***** This Solvent Polarity Index is an empirical scale based around the boundaries of tetramethylsilane (TMS) = 0.00 and Water = 10.00. Normalised and dimensionless, it is derived from spectroscopic measurements involving ‘solvatochromism’. See: Table A-1 Page 472 of Reichardt, C. (1988) Solvents and Solvent Effects in Organic Chemistry, VCH Publishers: Weinheim; and also Christian Reichardt, ‘Solvatochromic Dyes as Solvent Polarity Indicators’, Chem. Rev. 1994, 94, 2319-2358.

Using the rule of thumb identified in the book that “like dissolves like”, then a combination of markers such as structure, functional groups, and the ‘Polarity Index’ (PI) allows an initial solvent choice to be made. As a guide, the closer the value of the PI to that of the analyte and the matrix that retains it, the more compatible it may be; [compatibility may also be gauged using the dielectric constant value, the dipole moment or a combination of the two, which are also identified in the table]. However, solubility for an analyte in a solvent is obviously the first consideration!

Combinations of miscible solvents may allow effects of solubility and permeation to be extended for solid matrices that exhibit particular properties because of their mixed polarities. One example to illustrate this point is the use of a 1:1 (v/v) hexane : acetone miscible solvent mixture, for the extraction of a wide variety of organic contaminants present in soils and biological materials because of its ability to not only dissolve a range of organic compounds of varying polarity but to also ‘wet’ a wide range of matrices.

When an aqueous system is being considered solely as the solvent, then one of the following may also be of interest:

High purity (HP) water

HP Water set to a selected pH using acid, alkali or buffer salt reagents

HP Water containing selected salt electrolytes

HP Water containing a complexing agent.

<u>Extraction methods available when using a suitable solvent</u>

As has been shown in Chapter 3 and section 3.6 in the book, a range of extraction methodology is available for solid and liquid samples. For consideration, the following EPA standard methods /approaches are presented:

Solid samples may be extracted with an appropriate solvent system [including, as examples, hexane-acetone (1:1) or methylene chloride-acetone (1:1)] using Method 3540 (Soxhlet extraction), Method 3541 (automated Soxhlet extraction), Method 3545 (pressurized fluid extraction), Method 3546 (microwave extraction), Method 3550 (ultrasonic extraction), or other appropriate techniques using validated peer-assessed methodology. In each case the solvent system chosen should provide the highest extraction efficiency possible; preferably as close to 100% as possible, both verifiable and reproducible.

Aqueous samples may be extracted (for example, at neutral pH with methylene chloride) using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extraction), Method 3535 (solid-phase extraction), or other appropriate techniques using validated peer-assessed methodology. In each case the solvent system chosen should provide the highest extraction efficiency possible; preferably as close to 100% as possible, both verifiable and reproducible.