



ANALYTICAL CHEMISTRY BY OPEN LEARNING

Sample Pretreatment and Separation

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Analytical Chemistry

This series of texts is a result of an initiative by the Committee of Heads of Polytechnic Chemistry Departments in the United Kingdom. A project team based at Thames Polytechnic using funds available from the Manpower Services Commission 'Open Tech' Project has organised and managed the development of the material suitable for use by 'Distance Learners'. The contents of the various units have been identified, planned and written almost exclusively by groups of polytechnic staff, who are both expert in the subject area and are currently teaching in analytical chemistry.

The texts are for those interested in the basics of analytical chemistry and instrumental techniques who wish to study in a more flexible way than traditional institute attendance or to augment such attendance. A series of these units may be used by those undertaking courses leading to BTEC (levels IV and V), Royal Society of Chemistry (Certificates of Applied Chemistry) or other qualifications. The level is thus that of Senior Technician.

It is emphasised however that whilst the theoretical aspects of analytical chemistry can be studied in this way there is no substitute for the laboratory to learn the associated practical skills. In the U.K. there are nominated Polytechnics, Colleges and other Institutions who offer tutorial and practical support to achieve the practical objectives identified within each text. It is expected that many institutions worldwide will also provide such support.

The project will continue at Thames Polytechnic to support these 'Open Learning Texts', to continually refresh and update the material and to extend its coverage.

Further information about nominated support centres, the material or open learning techniques may be obtained from the project office at Thames Polytechnic, ACOL, Wellington St., Woolwich, London, SE18 6PF.

How to Use an Open Learning Text

Open learning texts are designed as a convenient and flexible way of studying for people who, for a variety of reasons cannot use conventional education courses. You will learn from this text the principles of one subject in Analytical Chemistry, but only by putting this knowledge into practice, under professional supervision, will you gain a full understanding of the analytical techniques described.

To achieve the full benefit from an open learning text you need to plan your place and time of study.

- Find the most suitable place to study where you can work without disturbance.
- If you have a tutor supervising your study discuss with him, or her, the date by which you should have completed this text.
- Some people study perfectly well in irregular bursts, however most students find that setting aside a certain number of hours each day is the most satisfactory method. It is for you to decide which pattern of study suits you best.
- If you decide to study for several hours at once, take short breaks of five or ten minutes every half hour or so. You will find that this method maintains a higher overall level of concentration.

Before you begin a detailed reading of the text, familiarise yourself with the general layout of the material. Have a look at the course contents list at the front of the book and flip through the pages to get a general impression of the way the subject is dealt with. You will find that there is space on the pages to make comments alongside the

text as you study—your own notes for highlighting points that you feel are particularly important. Indicate in the margin the points you would like to discuss further with a tutor or fellow student. When you come to revise, these personal study notes will be very useful.

II When you find a paragraph in the text marked with a symbol such as is shown here, this is where you get involved. At this point you are directed to do things: draw graphs, answer questions, perform calculations, etc. Do make an attempt at these activities. If necessary cover the succeeding response with a piece of paper until you are ready to read on. This is an opportunity for you to learn by participating in the subject and although the text continues by discussing your response, there is no better way to learn than by working things out for yourself.

We have introduced self assessment questions (SAQ) at appropriate places in the text. These SAQs provide for you a way of finding out if you understand what you have just been studying. There is space on the page for your answer and for any comments you want to add after reading the author's response. You will find the author's response to each SAQ at the end of the text. Compare what you have written with the response provided and read the discussion and advice.

At intervals in the text you will find a List of Objectives which are based on the material you have just read. The Objectives will give you a checklist of tasks you should then be able to achieve.

You can revise the Unit, perhaps for a formal examination, by re-reading the Objectives, and by working through some of the SAQs. This should quickly alert you to areas of the text that need further study.

At the end of the book you will find for reference lists of commonly used scientific symbols and values, units of measurement and also a periodic table.

Study Guide

Welcome to this Unit on sample pretreatment, separation, and preconcentration! In the Unit we shall study ways in which raw samples received for analysis are converted into a form suitable for making useful measurements. If you have had any previous analytical experience, I am sure you have already found that it is most unlikely that you could analyse a sample in *exactly* the form in which you received it. Virtually every analytical procedure calls for some degree of sample pretreatment. In the simplest situation, this might merely involve, say, the filling of a sample cell. On the other hand, a complex and tricky sequence of operations might be called for, perhaps involving grinding a solid sample to give a fine powder, leaching this with acid, fusing the residue, taking the product up in acid, then complex separations and preconcentrations on the resulting solution, together with derivatisation steps at one or more stages.

In many analyses, possibly in most, the sample pretreatment stage is the longest part of the procedure, and the one requiring the highest degree of manipulative skill from the analyst. It is very important, therefore, that you appreciate the need to develop appropriate skills and knowledge in the field of sample pretreatment, separation, and preconcentration. The purpose of this Unit is to help you to acquire such skills.

The basic structure of the Unit is as follows. Part 1 reviews the major stages of an analysis and the position of pretreatment and separation in the overall analysis. Part 2 will be concerned with a general survey of a number of preliminary sample pretreatments which might

precede other processes to be discussed later. We then go on to look at methods for dissolution and opening-out of samples, ie methods of obtaining a solution of the analyte (probably an aqueous solution of a species of interest in an appropriate chemical form) from either inorganic or organic matrices (Parts 3 and 4). In Parts 5 and 6 we study ways in which the analyte (now assumed to be in solution) is beneficially converted into a different chemical form, either to make its determination possible or more efficient, or to aid its separation, preconcentration, or further pretreatment. In Part 7 we introduce the topics of separation and preconcentration, initially in a very general way, and then review very briefly a wide selection of separation and preconcentration techniques. In Parts 8 to 10 we consider in more detail a number of the more important separation techniques including solvent extraction, ion exchange, adsorption and desorption, precipitation and co-precipitation, and use of vapour-phase equilibria. Perhaps I should point out at this stage that the most widely used group of separation techniques, namely chromatography and electrophoresis, although touched upon from time to time, will not formally be covered in this Unit. This subject is so large that five individual ACOL Units are devoted entirely to it.

Inevitably, I must assume that you, the reader, will have a certain level of preknowledge of chemical principles before you embark on the Unit. Most of these will be familiar to you if you have reached GCE 'A' level standard in chemistry. Where there is any doubt, I have provided exercises with remedial instruction in the responses, together with suitable references where necessary. In this way, you should be able to make good any deficiencies in your chemical background. On this point, you will find that the contents of *ACOL; Classical Methods*, especially those parts concerned with equilibria, complex formation, and precipitation, will be relevant to this Unit. Since pretreatment implies that an analysis will follow, we also refer from time to time to various common analytical measurements. No detailed knowledge of these will be assumed, but I shall assume that you have an interest in chemical analysis, and will therefore have a current awareness knowledge of at least some such techniques.

In studying this Unit, you will, no doubt, wish to consult textbooks and other references. Although there are some excellent coverages of such topics as solvent extraction and ion-exchange, some of the

less common separation techniques, as well as much of the material on sample pretreatment, is rather scattered in the literature and is not very well covered in general textbooks on chemical analysis, where the emphasis is generally on more specific analytical (ie measurement) techniques. References are provided, but for some general textbooks that cover most (but not all) of this Unit, perhaps I could direct your attention to texts by Skoog and West and by Fifield and Kealey (see Bibliography).

A multiple choice test on the contents of the Unit itself follows this Study Guide and Bibliography. I want you to have a go at this test before starting on the main Parts of the Unit, but I do want you to understand that the material being tested is that which is to be covered in the Unit. *Therefore do not be surprised or worried if you score a low mark or even zero, as you may well do* (indeed, if you were to get a particularly high mark, I should wonder whether you need to study the Unit at all!) However, record your mark, whatever it is, in the place indicated, and then after you have completed your study of the Unit, I shall ask you to come back and do the test again. I hope that on your second attempt your mark will have substantially improved, the extent of the improvement being a measure of the amount that you have learned from the Unit.

Good luck with the Unit!

Preliminary Multiple-choice Pre- and Post-test

Work through this test before you start on the Unit and then repeat the test on completion of the Unit. Record your marks for both attempts in the boxes provided at the end of the test. Your first mark is likely to be low, but I hope that the mark for your second attempt will be significantly higher. The improvement in the mark obtained will serve as a rough guide to the extent to which you have benefited from your study of the Unit.

For each question simply select the most suitable response and note it on a *separate* sheet of paper. To mark the test, compare your selection of responses with those at the end of the test. Where they agree, ie where your response is correct, *score +1 mark*; where they disagree, ie where your response is incorrect, *score -1/3 mark*. If for any question you have not selected any response, *score 0 mark*. Finally, count up your marks, remembering to subtract the 1/3 mark for wrong responses. Your total mark will be out of 20.

1. The term 'leaching' means:

- (a) extraction of lipophilic compounds from an aqueous solution into an organic solvent;
- (b) heating a solid sample with an electrolyte to form a melt, which is then dissolved in dilute acid;
- (c) extraction of a soluble component from a solid sample by using a specific solvent or reagent mixture;

- (d) exhaustive oxidation of an organic matrix to release the elements therein into an aqueous solution for inorganic analysis.
2. A simple procedure for obtaining an aqueous solution for determination of Al and Si in a finely powdered aluminosilicate would involve:
- (a) dissolution of the powder in boiling concentrated HF to which NaF had been added (to raise the boiling point);
 - (b) exhaustive treatment by boiling the sample with the acids, HNO_3 , H_2SO_4 and HClO_4 in that order;
 - (c) dissolution in a hot concentrated solution of NaOH;
 - (d) fusion with Na_2CO_3 and dissolution of the clear melt in dilute HCl containing a little H_2O_2 .
3. Metallic gold is soluble in:
- (a) concentrated H_2SO_4 plus concentrated H_3PO_4 (1 : 4 v/v);
 - (b) concentrated HCl plus concentrated HNO_3 (3 : 1 v/v);
 - (c) concentrated HClO_4 ;
 - (d) concentrated H_2SO_4 plus concentrated HF (1 : 1 v/v).
4. A Kjeldahl flask is:
- (a) a sealed conical flask containing oxygen and used for dry-ashing small amounts of organic material held in a platinum basket;
 - (b) a sealed flask used inside a bomb for reductive fusions with sodium metal for halide determinations;
 - (c) a special flask that can be mounted in a radiofrequency field for low temperature dry ashings;
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- (d) a round-bottomed, long-necked pyrex flask used for wet-ashing organic material.
5. In dry-ashing a sample of salted fish for a trace determination of lead, the following precaution is particularly important:
- (a) a platinum or nickel crucible must be used to avoid adsorption of Pb on, say, a glass surface;
 - (b) the temperature should not be too high or else the Pb is volatilised;
 - (c) the sample must be ashed in an oxygen-rich atmosphere to increase the oxidisability of the material in the presence of NaCl;
 - (d) the sample must be heated to at least 700 °C to ensure complete oxidation.
6. A common way of improving the volatility of fatty acids for analysis by gas-liquid chromatography is:
- (a) to reduce them to the corresponding hydrocarbons;
 - (b) to convert them into their trimethylsilyl esters;
 - (c) to convert them into their methyl esters;
 - (d) to pyrolyse them.
7. The term *chelate effect* is used to describe:
- (a) the increase in stability of a metal complex due to the formation of a ring structure on complex formation, when compared with that of a similar metal complex where no ring is formed;
 - (b) the increase in stability of the resulting metal complex observed by ensuring that a 'hard' metal ion is complexed with a 'hard' ligand, and likewise for 'soft' metal ions and ligands;

- (c) the different stabilities observed for metal complexes differing only in ring sizes formed on complexation;
 - (d) the different stabilities of metal complexes, which differ only with respect to the presence or otherwise of large groups adjacent to the complexing atoms in the organic ligand.
8. The true stability constant of a metal complex is, to a first approximation:
- (a) dependent on pH, with a sigmoid relationship;
 - (b) linearly dependent on pH, the slope being determined by the stoichiometry of the complex;
 - (c) independent of pH;
 - (d) dependent on pH only if the ligand is a weak acid.
9. A batch separation technique is most likely to be encountered when:
- (a) a preconcentration is to be performed involving a particularly large preconcentration factor;
 - (b) the species to be separated have similar, but not identical, distribution ratios between the two phases involved;
 - (c) extreme differences exist in the separability of the species to be separated;
 - (d) the components of large amounts of material are to be separated.
10. Dialysis is a separation technique involving:
- (a) differential diffusion, on the basis of size, of molecules in solution, through a semi-permeable membrane, separating two liquid phases;
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- (b) differential rates of migration of molecules in solution under the influence of an intense centrifugal force;
- (c) differential rates of migration of charged particles under the influence of an electric field;
- (d) fractionation of molecules in solution on the basis of molecular size by means of a molecular sieve (a solid material containing pores of controlled size).

11. Solvent extraction might be useful for:

- (a) preconcentrating traces of F^- in water (the pH is adjusted to produce non-ionic HF, which is then extracted into a polar organic solvent);
- (b) resolution of a mixture of amino-acids on the basis of their differing solubilities in organic solvents at different values of pH;
- (c) separation of the alkali metals on the basis of pH control and the differing stabilities of their complexes with a suitable organic ligand (eg 8-hydroxyquinoline);
- (d) preconcentrating traces of a non-polar organic compound, present in a large volume of water, into a small volume of organic solvent.

12. Two metal ions form extractable neutral chelate complexes with the same organic ligand, although the stabilities of these complexes are very different. The metal ions are thus separable by solvent extraction of these complexes provided:

- (a) the pH of the aqueous phase is carefully adjusted to a suitable value;
 - (b) the concentration of the ligand is carefully adjusted to a suitable value;
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- (c) the aqueous:organic-phase volume-ratio is carefully adjusted to a suitable value;
 - (d) a carefully chosen masking agent is added to the aqueous phase.
13. Ferrous and ferric ions can be separated by solvent extraction, by:
- (a) extracting the ferric ions into diethyl ether from 6*M*-HCl, leaving the ferrous ions in the aqueous phase;
 - (b) extracting the ferric ions into trichloromethane as ion-pairs formed between the *o*-phenanthroline complex of Fe^{3+} and ClO_4^- , leaving the ferrous ions in the aqueous phase;
 - (c) extracting the ferrous ions into diethyl ether from a concentrated aqueous solution of ammonium thiocyanate, leaving the ferric ions in the aqueous phase;
 - (d) extracting the ferrous ions into trichloromethane as ion-pairs formed between the neocuproine complex of Fe^{2+} and NO_3^- , leaving the ferric ions in the aqueous phase.
14. In order to fractionate a mixture of organic compounds in aqueous solution into neutral extractable, acidic extractable, basic extractable, and non-extractable compounds, by extraction into an organic solvent, you would:
- (a) check that the aqueous phase is neutral and extract. Then extract solutes from the resulting organic phase (i) with an acidic, (ii) with an alkaline aqueous phase;
 - (b) acidify the sample and extract. Then make the aqueous phase alkaline and re-extract. Then back-extract solutes from the organic phase obtained from the first extraction with an alkaline aqueous phase;

- (c) make the sample alkaline and extract. Then acidify the aqueous phase and re-extract. Then back-extract solutes from the organic phase obtained from the first extraction with an alkaline aqueous phase;
 - (d) acidify the sample and extract. Then make the aqueous phase alkaline and re-extract. Then back-extract solutes from the organic phase obtained from the first extraction with an acidic aqueous phase.
15. Increased cross-linking in an ion-exchange resin:
- (a) increases its affinity towards ions of smaller solvated radius;
 - (b) increases its affinity towards ions of higher charge;
 - (c) increases its selectivity towards ions of higher charge;
 - (d) increases its selectivity towards ions of smaller solvated radius.
16. The best conditions for preconcentrating trace transition- and heavy-metal ions in sea water by ion-exchange are:
- (a) to buffer the solution to pH 6–8, pass it through a chelating ion-exchange resin in the H^+ form and then collect the preconcentrated ions by eluting them with $2M-HNO_3$;
 - (b) to pass the solution through a strong cation-exchange resin in the Na^+ form, ash the resin and take up the residue in $2M-HNO_3$;
 - (c) to pass the solution through a strong cation-exchange resin in the H^+ form, collect the preconcentrated ions by eluting them with $2M-HNO_3$;
 - (d) to make the solution $12M$ in HCl pass it through a strong anion-exchange resin in the Cl^- form, and collect the ions by elution with water.
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17. The best conditions for separating the components of a mixture of amino-acids by ion-exchange would be:

- (a) to retain the acids as cations on a cation-exchange resin and then elute the acids in sequence by using a series of buffers of gradually decreasing pH;
- (b) to retain the acids as anions on an anion-exchange resin and then elute the acids in sequence by using a series of buffers of gradually increasing pH;
- (c) to retain the acids as cations on a cation-exchange resin and then elute the acids in sequence by using a series of buffers of gradually increasing pH;
- (d) to convert the acids into their zwitterionic forms when they can be retained on either a cation- or an anion-exchange resin, then elute the acids in sequence, either by increasing the pH (cation exchange) or decreasing the pH (anion exchange).

18. Adsorption involves the reversible retention of molecules from the gaseous or solution phase:

- (a) within the bulk of a solid or liquid phase by mechanisms akin to solvent extraction;
- (b) on the surface of a solid phase by physical or chemical means;
- (c) in the pores of a porous solid medium permeable to small molecules, no chemical interactions being involved;
- (d) within the crystal structure of a solid by means of gaps in the crystal lattice of similar size and shape to the adsorbed molecules.

19. Coprecipitation:

- (a) is the only known method for preconcentrating anions in water;
- (b) can be used for the non-specific preconcentration of material in general in aqueous solution;
- (c) is a nuisance in gravimetry, where it often causes contamination of precipitates;
- (d) can be used for the gravimetric determination of trace metal-ions in sea water.

20. Reduction with NaBH_4 will cause the following elements, in inorganic form in aqueous solution to be converted into a volatile form:

- (a) Cl, Br, I;
- (b) Sn, Hg, Zn;
- (c) Ru, Os, Cr;
- (d) As, Se, Te.

Answers

Score +1 for each correct response, $-1/3$ for each incorrect response and zero for each missing response. Add up your marks, remembering to subtract any negative marks. The maximum score is 20.