CHAPTER 4: SAMPLES AND SAMPLE PRETREATMENT

4.1 INTRODUCTION

The quality of data generated in an investigation is only as good as the weakest point in the chain of events from sampling to the treatment of final data. The final errors of the analysis are the result of compounded errors which have been picked up throughout the analysis trail (Howard and Stratham, 1993). It is therefore important to minimize errors at each step of analysis. This chapter focuses on the sample preparation steps from description of samples, preservation and storage, cleaning of apparatus, sample pretreatment to wet acid digestion used in this study to ensure minimal errors.

4.2 SAMPLES

4.2.1 PGMs and gold concentrates

Platinum ore is mined from the Merensky and the UG2 reefs, the two main platinum-bearing reefs in South Africa. Depending on the mineralogy of the ore, the PGM recovery process has to go through four complicated stages of concentration, smelting, base metals removal, and precious metals refining. During concentration process, the ore is ground into fine particles with the aim of liberating and recovering the mineral particles in the form of a concentrate by froth flotation. From this, a concentrate is obtained, which is a form of the ore which has had the majority of its base components removed. The benefit of which

is the reduction in weight for transportation. PGMs and gold concentrates used in this study were obtained in a similar way and included AMC QC01, LMC QC03, LUC QC02 and PPC QC02 with metal constituents obtained by NiS fire assay technique followed by ICP-OES determination as shown in table 4.1 and 4.2.

Table 4.1 PGMs and gold values and limits for a single analysis of PGMs and gold concentrates obtained by NiS fire assay ICP-OES technique

	Pt $g\ t^{-1}$	Pd $g\ t^{-1}$	Rh $g\ t^{-1}$	Ru $g\ t^{-1}$	Ir $g\ t^{-1}$	Au $g\ t^{-1}$
Lower limit	84.42	54.43	10.53	14.69	3.06	3.6
AMC QC 01	88.28	56.71	11.07	15.63	3.34	4.22
Upper limit	92.14	58.99	11.61	16.57	3.62	4.84
Lower limit	126	144	26.1	36.9	9.1	3.7
LUC QC 02	131	153	28.6	38.6	9.7	4.4
Upper limit	136	162	31.1	40.3	10.3	5.1
Lower limit	139	62.8	8.7	16.7	2.8	9.8
LMC QC 03	145	65.4	9.1	17.7	3.1	10.7
Upper limit	151	68.0	9.5	18.7	3.4	11.6
Lower limit	37.4	34.3	2.2	2.1	0.6	3.9
PPC QC 02	39.0	36.3	2.5	2.3	0.7	4.3
Upper limit	40.7	38.2	2.8	2.6	0.8	4.7

4.2.2 Grass, lichens, leaves and tree trunk samples

Grass samples were sampled from Kruger Park in north east of South Africa. Lichen samples were collected from within the University of the Witwatersrand in Johannesburg, South Africa. Leaves and tree trunk samples were collected from Welkom, south west of Johannesburg.

Table 4.2 Base metal values and limits for a single analysis of PGMs and gold concentrates obtained by NiS fire assay ICP-OES technique

	Ni %	Cu %	Co %	Fe %	S %	Cr2O3 %
Lower limit	3.53	2.15	0.085	16.20	8.32	0.95
AMC QC 01	3.63	2.22	0.093	16.76	9.32	0.98
Upper limit	3.73	2.29	0.101	17.32	10.32	1.01
Lower limit	3.66	2.39	0.07	13.06	7.86	4.02
LUC QC 02	3.90	2.55	0.08	13.80	8.02	4.32
Upper limit	4.14	2.71	0.09	14.54	8.18	4.62
Lower limit	7.31	4.18	0.11	21.22	17.64	0.34
LMC QC 03	7.59	4.28	0.12	21.92	18.10	0.39
Upper limit	7.87	4.38	0.13	22.62	18.56	0.44
Lower limit	3.29	1.87	0.10	16.1	8.82	0.20
PPC QC 02	3.40	1.92	0.11	16.7	9.06	0.22
Upper limit	3.51	1.97	0.12	17.2	9.30	0.24

4.3 PRESERVATION AND STORAGE CONDITIONS

Sample collection to analysis takes time and sample preservation and storage is required to minimize deterioration of the sample which occurs during the intervening time. It is rarely possible to avoid storage completely but, as most problems increase with time, every effort should be made to carry out analysis as soon as possible after obtaining the sample or to ensure sample stability during the intervening time.

4.3.1 Solid samples

Storage of solid samples presents less of a problem than is the case with solutions. The concentrates samples, ground grass, lichens, leaves and tree trunk samples were thoroughly dried to minimize deterioration from soil organisms and

moisture. Drying was carried out slowly, at temperatures below 100ºC. Conventional ovens were used for this purpose.

The dried solid samples were stored in plastic containers, poly(tetrafluoroethylene) (PTFE). This is because PTFE has low coefficient of friction that limits solid sample contamination due to mechanical abrasion of the container wall. The samples were kept at room temperature (23ºC).

4.3.2 Solutions

Both standards and slurry samples were present in solutions. All solutions were prepared in deionized water. Standards were acidified with 1% v/v HNO_3 (55%, Merck) to ensure that hydrolysis did not take place.

PTFE plastic containers were used to store solutions because of its high chemical stability. These containers were heated to 300ºC before use to help overcome the polymer problem of exuding low molecular weight compounds from surfaces of fresh materials. The use of glass apparatus was avoided to prevent loss of analytes through sequestering of metals on the glass surface. The standard solutions were refrigerated at 4^{o}C and fresh slurry solutions were used every time.

4.4 CLEANING OF APPARATUS

Sample containers and other glassware were cleaned with metal-free non-ionic detergent solution, rinsed with tap water, soaked in 50% HNO_3 acid for 12 hours and then rinsed with deionised water from a Milli-Q-water purification system as recommended by Arienzo and Scrudato, 2001. All sample containers were rinsed again with deionised water prior to use. All blanks were subjected to similar sample preparation and analytical procedures. All chemicals were of analytical grade obtained from Sigma-Aldrich, Industrial Analytical and Merck.

4.5 SAMPLE PRETREATMENT STEPS

4.5.1 Dusting

Grass, lichens, leaves and tree trunk samples were thoroughly dusted using a dusting brush to remove all the dust on their surfaces before drying.

4.5.2 Drying and homogenization

Drying of the organic materials (grass, lichens, leaves and tree trunk samples) was done to ensure accurate and reproducible weighing. A conventional oven drying technique was used. The samples were put in the oven and dried at 100ºC until constant weight was achieved. The dried samples were thoroughly mixed to homogenize them, put in vials and kept in a dessicator to guarantee that there was no take up of water from the atmosphere.

4.5.3 Sample grinding

Grinding samples for slurry analysis is a critical step in the sample preparation procedure. Previous studies show that atomization efficiency in the plasma is greatly improved at particle size of < 5 - 10 µm that ensures that the slurry has similar transport properties to an aqueous solution.

Various grinding methods have been used for the preparation of slurries including: micronizing mills (Fuller *et al.*, 1981); rotary disc mills (Halics and Brenner, 1995); the 'bottle and bead' method (Williams *et al.*, 1987, Jarvis, 1992, Jarvis and Williams, 1989) and rotary grinders with tungsten carbide utensils (Verbeek and Brenner, 1989). For most samples it is best to pulverize using sealed bowl pulverizers, ring and puck type (sometimes called swing mills), or 'flying saucer' type mills (such as the lab technics ones). Ring and pipe mills usually provide the finest pulp (Ebdon *et al.*, 1997). Brooks (2001), recommends caution when using 'flying saucer' type pulverizer, he showed an example of up to 35% difference taken from samples prepared using this type of pulverizer. He theorized that minerals with high specific gravity such as Au or the PGMs segregate and settle to the bottom of the bowl, particularly a problem if the sample is pulverized for too long a time period.

The use of contra-rotating disc pulverizers is not recommended because minerals are segregated based on density. Improper mat rolling with improper mat sub

sampling may further aggravate the situation. The heavy minerals segregate on the mat surface, and have an overlying layer of the lower grade pulp. Use of "wash dirt" or cleaner sand to clean process equipment between samples is suggested to avoid cross contamination. Contamination from sample comminution equipment also can occur (Hoffman and Dunn, 1999).

Jarvis K.E and Williams (1989) demonstrated the general effectiveness of the 'bottle and bead' method for grinding a range of geological materials to a maximum particle size of < 5 µm. However in this method, 16 hours grinding is required to get the particles to < 5µm in diameter.

Planetary mono mill 'pulverisette 6' was used in this study partly based on the availability of instrumentation but mainly because of its quick dry and wet grinding capability of both inorganic and organic samples within reduced grinding times.

4.5.4 Particle Size Measurement

Sample grinding is succeeded by particle size distribution measurement. A number of techniques could be used for this and include coulter counter (geological materials, 7-10 µm), laser diffractometer (geological samples, < 2 µm, using particle size analyser) and photosedimentometer (geological samples, < 2 µm). Often the method by which the particle size is measured depends on

instrumentation available, so there is no rigid methodology to follow for a particular sample. For this study, Malverns Masters Sizer S instrument was employed on the basis of its ability to quantify particles over 0.05 µm – 900 µm range, allowing detection of both well dispersed and agglomerated material.

4.5.5 Slurry dispersion

A dispersing agent is required to keep the ground particles suspended and to prevent flocculation. Dispersion of slurry using stabilizing agents (dispersants or surfactants) is necessary to avoid coagulation (agglomeration) to obtain stable homogeneous slurry.

An ideal dispersing agent for slurry nebulization would introduce minimal contamination and have a viscosity close to water. Wide ranges of dispersing agents have been used (Jarvis, 1992). However, to date there has been no systematic study to evaluate their relative merits, and choice seems to be based on personal preference. Tetra sodium pyrophosphate ($Na_4P_2O_7$) was successfully used by Williams *et al.* (1987) in their initial feasibility study of slurry nebulization ICP-MS and has yielded good results in other studies for trace element determinations of geological materials (Jarvis, 1992, Jarvis and Williams, 1989).

Particles agglomeration and flocculation

Particles in dispersion may adhere to one another and form aggregates of successively increasing size, which may settle out under the influence of gravity. An initially formed aggregate is referred to as a 'floc' from the word flocculation and the process of its formation, flocculation. The 'floc' may or may not sediment or phase separate. If the aggregate changes to a much denser form, it is said to undergo coagulation. An aggregate usually separates out either by sedimentation (if it is more dense than the medium) or by creaming (if it is less dense than the medium).

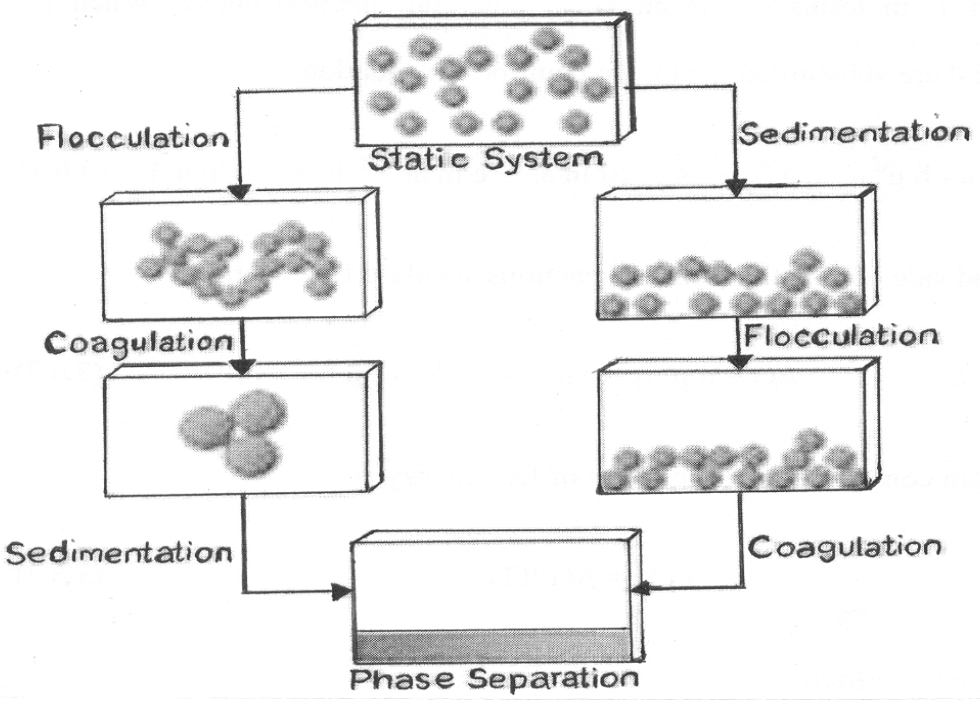


Figure 4.1 Schematic diagrams showing various mechanisms where stability could be lost in slurry dispersion

The terms flocculation and coagulation have been often used interchangeably. Usually coagulation is irreversible whereas flocculation can be reversed by the process of deflocculating.

DVLO theory

Derjaguin, Landau (1941), Verwey and Overbeek (1948) developed a theory which dealt with the stability of colloidal systems. DVLO theory suggests that the stability of a particle in solution is dependent upon its total potential energy function V_T. This theory recognizes that V_T is the balance of several competing contributions:

$$V_T = V_A + V_R + V_S \qquad (4.1)$$

V_S is the potential energy due to the solvent, it usually only makes a marginal contribution to the total potential energy over the last few nanometers of separation. Much more important is the balance between V_A and V_R, these are the attractive and repulsive contributions. They potentially are much larger and operate over a much larger distance

$$VA = -A/(12\pi D^2) \qquad (4.2)$$

Where A is the Hamaker constant and D is the particle separation.

The repulsive potential V_R is a far more complex function:

$$VR = 2\,\pi\,\varepsilon\,a\,\zeta^2\exp(-\kappa D) \qquad (4.3)$$

Where a, is the particle radius, π is the solvent permeability, κ is a function of the ionic composition and ζ is the zeta potential.

DVLO theory suggests that the stability of a colloidal system is determined by the sum of this Van der Waal attractive (V_A) and electrical double layer repulsive (V_R) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together (figure 4.2). But if the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact where they adhere strongly and irreversibly together.

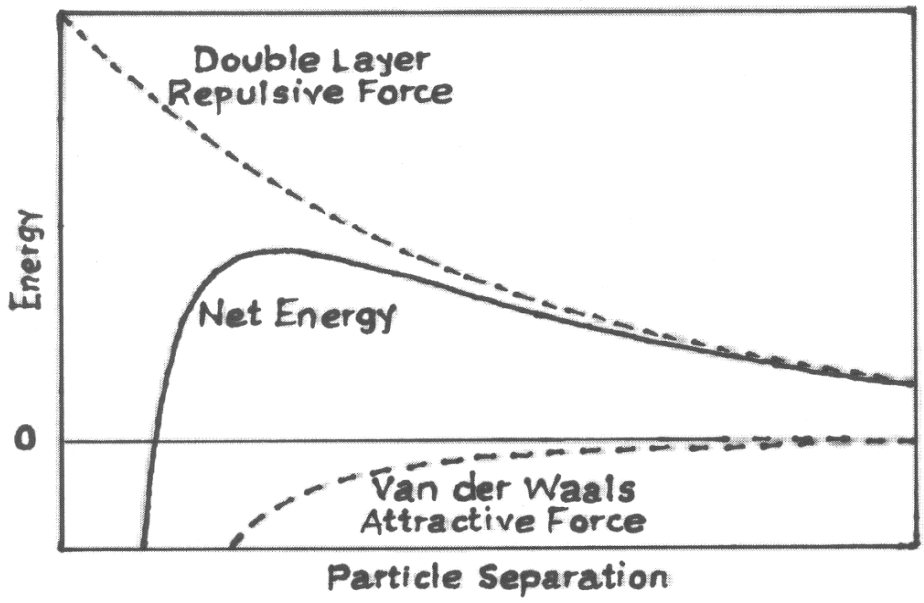


Figure 4.2 Schematic diagram of the variation of free energy with particle separation according to DVLO theory

Therefore if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However if repulsion mechanism does not exist then flocculation or coagulation will eventually occur.

If the zeta potential is reduced (e.g. in high salt concentrations), there is a possibility of a 'secondary minimum' being created, where a much weaker and potentially reversible adhesion between particles exists (figure 4.3). These weak flocs are sufficient not to be broken up by Brownian motion, but may disperse under an externally applied force such as vigorous agitation.

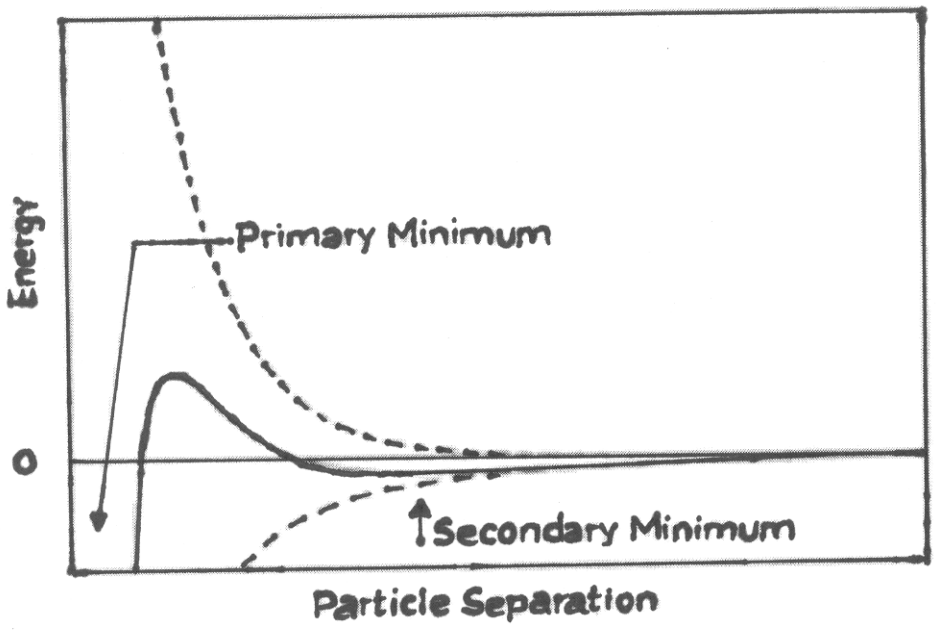


Figure 4.3 Schematic diagram of the variation of free energy with particle separation at higher salt concentrations showing the possibility of a secondary minimum

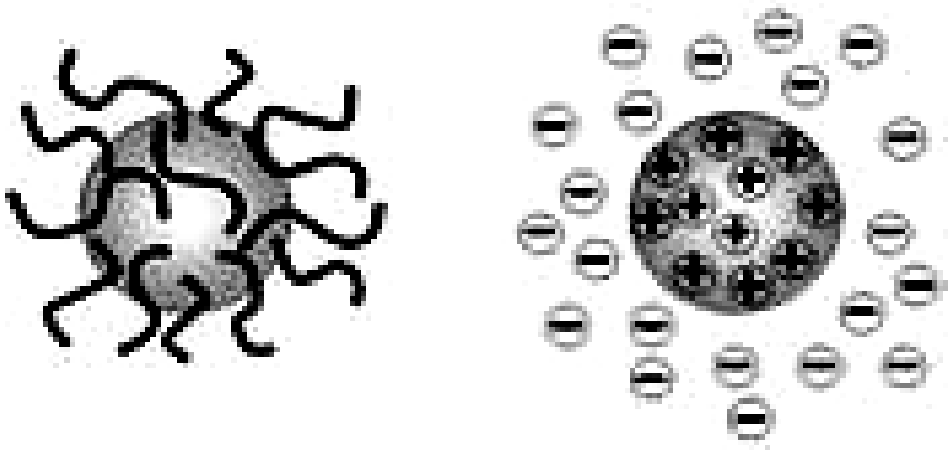
Therefore to maintain the stability of the colloidal system, the repulsive forces must be dominant. There are two fundamental mechanisms that affect dispersion stability, figure 4.4:

1. Steric repulsion – this involves polymers added to the system adsorbing onto the particles surface and preventing the particle surfaces from coming into close contact. If enough polymers adsorbs, the thickness of the coating is sufficient to keep particles separate by steric repulsions between the polymer layers, and at those separations the Van der Waals forces are too weak to cause the particles to adhere.

2. Electrostatic or charge stabilization – this is the effect on particle interaction due to the distribution of charged species in the system.

Each mechanism has its benefits for particular systems. Steric stabilization is simple, requiring just the addition of a suitable polymer. However, it can be difficult to subsequently flocculate the system if this is required, the polymer can be expensive.

Electrostatic or charge stabilization has the benefits of stabilizing or flocculating a system by simply altering the concentration of ions in the system. This is a reversible process and is potentially inexpensive.



(a) Steric repulsion (b) Electrostatic stabilization

Figure 4.4 Steric repulsion and electrostatic or charge stabilization

As discussed earlier, the addition of a dispersant causes the zeta potential to change and ultimately acts to stabilize the slurry. It changes the concentration of the potential determining ion by changing the surface potential of the particles according to Nernst equation. This alters the relative adsorption of ions on the surface of the slurry particles. Therefore, slurry is only stable when the zeta potential is high and significantly removed from the isolectric point (Gray and Williams, 1987). Different slurry dispersants were assessed as discussed in chapter six.

4.5.6 Stirring

Stirring ensures homogeneous distribution of the solid materials in the liquid phase and prevents sedimentation of particles. The concentrates contained magnetic, iron containing minerals such as magnetite (Fe_3O_4). The use of magnetic stirrer was therefore avoided because it would result in the removal of magnetic mineral phases, such as magnetite, during mixing (Gray and Williams, 1987) by migration and even adhesion of some slurry particles to the magnetic stirring bar. Slurry samples were agitated by placing sample bottles in ultrasonic baths before and during analysis to ensure that the slurry particles remained in suspension and well mixed.

4.6 DISSOLUTION OF SOLID SAMPLES

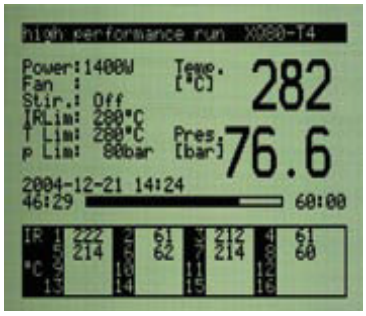
Wet acid digestion was used to convert the samples into solution for determination of total metal concentrations by ICP-OES. This was done for grass, lichens, leaves and tree trunk samples. Total metals concentrations for the concentrate samples were determined by NiS fire assay technique. Multiwave 3000 digestion instrument (Anton Paar GmbH) was used.

The sample and decomposition reagents (acids) were weighed into the reaction vessels, figure 4.5(a). The vessel seals were expanded by means of a seal-forming tool, replaced on the digestion vessels and closed with screw caps, figure 4.5(a). The pressure vessels were inserted into the rotor that was then placed in the Multiwave oven.

A built-in microcontroller that controls the instrument was used to define the decomposition or digestion program, to store the sample identity, method and other relevant information on the reaction process, figure 4.5(b). A pressure rate of 0.5 bars/second at a pressure of 20 bars and infra red radiation of 180º C was used for digestion.

The digestion programs used for digestion of the samples are shown in tables 4.2(a) and 4.2(b) for grass and lichens samples and leaf and tree trunk samples respectively.

(a)



(b)

(c)

(d)

Figure 4.5 (a) Lip-type vessel seals that allow hematic closure of reaction vessels (b) Built-in micro-controller software for Multiwave 3000 sensor (c) Multiwave 3000 sensor (d) Air gap design of vessel casing for cooling

Table 4.3 Multiwave 3000 digestion program used for decomposition of grass and lichen sample

Power (Watts)	Ramp (min)	Hold (min)	Fan speed
1200	15	30	1
Cooling	Cooling	20	2

Table 4.4 Multiwave 3000 digestion program used for decomposition of leaves and tree trunk samples

Power (Watts)	Ramp (min)	Hold (min)	Fan speed
1200	10	10	1
Cooling	Cooling	20	2

The operating pressure and decomposition temperatures were recorded simultaneously by means of a no-contact pressure/temperature sensor, figure 4.5 (c). Precise control of the temperature is essential for reproducible results. A temperature probe immersed in one reference vessel and an infrared sensor for sensing each vessel were employed for this purpose. The recorded values were transmitted to the built-in microcontroller. The microcontroller regulates the temperature and pressure within safety limits by decreasing the heating rate or stopping heating.

The cooling system was employed to generate a cooling air flow between the reaction vessels and the jacket and helped to prevent excessive thermal stress on the rotor and vessels during digestion, figure 4.5(d). The vessels were cooled down as soon as digestion was completed.

The digested samples were quantitatively transferred into volumetric flasks and the final volume adjusted to the mark with deionized water.

Conclusion

To state that good sampling practice is important and that the samples should be representative of material to be analyzed may at first seem to be stating the obvious. However, analysis problems start with experimental design and sampling. If these two steps are outside the control of the analyst no amount of analytical skill will recover useful results from poorly treated, preserved and stored samples.

The next chapter outlines the specific experimental procedures used for precise sample preparations required before sample introduction into the analytical instruments.