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APPENDICES

Appendix A

Phase Present

Phases present of samples were detected by X-ray diffractometer (XRD). XRD is an instrument for studying crystalline (and non crystalline) materials by measuring the way in which they diffract X-rays of known wavelenght(Cullity, 1969). The essential features of a diffractometer are shown in Fig. 36. A powder specimen C, in the form of a flat plate is supported on a table H, which can be rotated about an axis O perpendicular to the plane of the drawing.

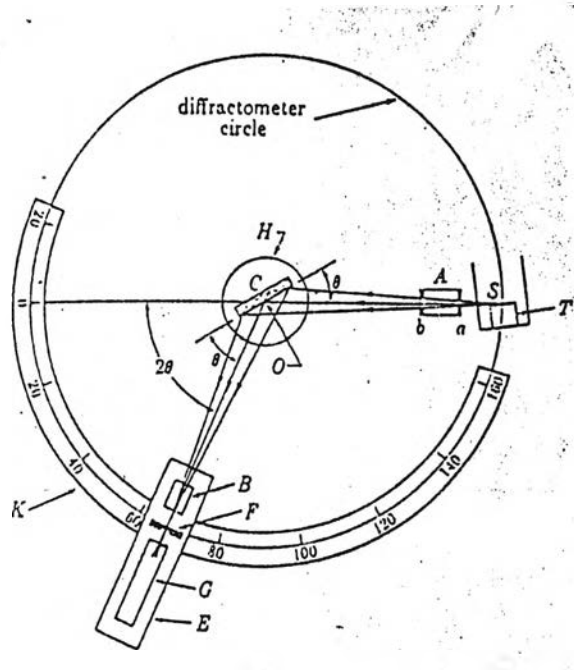


Fig. 38. Schematic of X-ray diffractometer.(Cullity, 1969)

The X-ray source is S , the line focal spot on the target T of the X-ray tube; S is also normal to the plane of the drawing and therefore parallel to the diffractometer axis O. X-rays diverge from this source and are diffracted by the specimen to form a convergent diffracted beam which comes to a focus at the slit F and then enters the counter G. A and B are special slits which define and collimate the incident and diffracted beam.

The receiving slits and counter are supported on the carriage E , which may rotate about the axis O and whose angular position 2O may be read on the graduated scale K. The supports E and H are mechanically coupled so that a rotation of the counter though 2θ degrees is automatically accompanied by rotation of the specimen through 2θ degrees.

When a randomly orientated aggregated of small crystal fragments (powder) is irradiated with a monochromatic beam of X-ray, the various planes of atoms will diffract the X-ray beam at angles determined by the spacing between the planes(d), according to the Bragg law,

$$n\lambda = 2d\sin\theta$$

where θ is the diffraction angle for lattice spacing, is the wavelength of the X-ray, and n is an integer (Reed, 1989). These diffracted beams are recorded on film placed

appropriatedly around the sample or by a scanning detector. The identification of phase is accomplished by comparing the d-spacings and relative intensities of the sample material with reference data for known materials.

To detect the phase present in this experiment, samples were dried and ground into fine powder in a porcelain mortar. The powders were compacted in a recess of plates. These plates were then inserted in the XRD specimen holder. XRD was run with copper K radiation and Ni filter. The scaning speed was 2° per min.

Appendix B

Infrared Spectrophotometry

Infrared (IR) radiation is electromaagnetric radiation (EMR). The infrared region starts at a wavelenght of about 0.7 µm and end at a wavelength of about 500µm. Infrared absorption occurred when the frequency of the alternating electric field that is associated with the incident radiation matches a possible change in a vibrational or rotational frequency of the absorbing molecule . When a match occurs, EMR can be absorbed by the molecule causing a change in the amplitude of vibration or a change in the rate of rotation.

In order for electromagnetic radiation to be absorbed by a molecule, it is necessary for the molecule to undergo a change of dipole moment during the absorption.If no change in the distribution of charge in the molecule occurs, the varying charge in the electric component of the radiation has nothing with which to interact and can not transfer energy to the molecule .Molecule that have a completely symmetrical charge distribution and in which no change in dipole momemt occures when the molecule vibrates with a different amplitude or

rotates at a different rate do not absorb infrared radiation. Substances that are transparent to infrared radiation are primarily monoatomic homonuclear diatomic gas such as He, Ne, Cl_2, N_2 and O_2. Nearly all other substances absorb radiation in the infrared region.

As is the case with electron level, rotational and vibrational levels are quantized. Classical physics is often used to provide quantitative descriptions of vibrational energenic levels with simple diatomic and triatomic,molecules. The nuclei are asumed to be known masses that are connected to each other by springs. The springs represent chemical bonds between ths atoms. Either harmonic or anharmonic oscillation can be assumed.

Because most analytical samples are in the liquid or solid state, the analyst is primarily concerned with changes in vibrational levels. Molecular vibrations are categorized as either stretching or bending vibrations. A stretching vibration corresponds to an oscillation along the internuclear axis.

In a molecule all of the possible vibrations or rotations (if a change in diapole moment occurs) can individually be reponsible for an absorptive band. Because many possibilities for a particular molecule can exist,

typical infrared spectra contain many absorptive bands . That is quite different from ultraviolet-visible spectra in which few absorptive bands are observed for a single compoud. The frequencies at which the absorptive band occurs are dependent upon many factors including the relative masses and polarities of the nuclei, the strenghts of the bonds in the molecule, and the number of atoms in the molecule. Additionally interactions (coupling) between different vibrations within the same molecule can occur. Theoretically no two compounds, with the exception of optical isomers, have identical infrared spectra. Consequently, infrared spectrophotometry is particularly useful for qualitative analysis.

The apparatus that is used for infrared spectrophotometry consists of the same types of components that are used for ultraviolet-visible spectrophotometry. In most cases the order of the components is altered from that of most ultraviolet-visible spectrophotometers. A block diagram of the major components in an infrared spectrophotometer is shown in Fig.39 . Most infrared spectrophotometers are double-beam instruments.

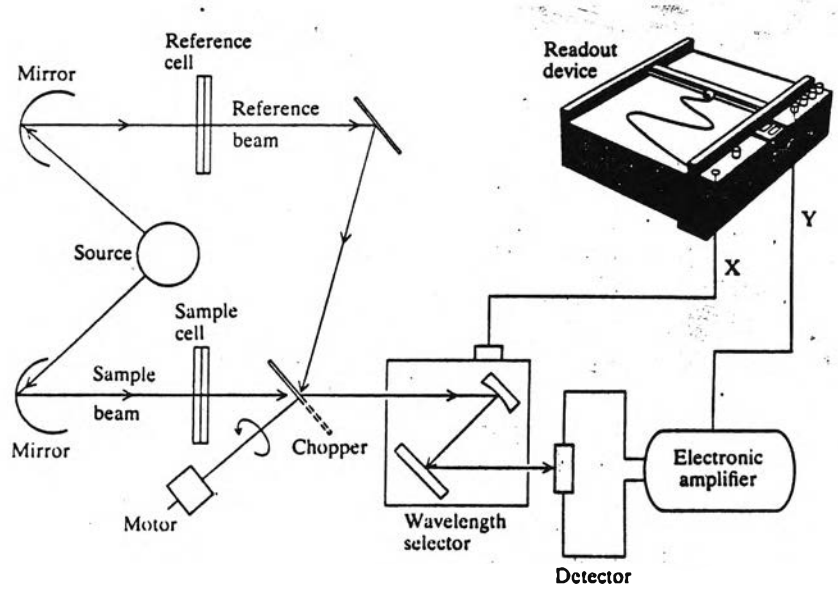


Fig.39 A block diagram of an infrared spectrophotometer.The arrows indicate the direction of radiative flow.

(Robert, 1987)

To detect IR spctra by mulls technique for this experiment, 2 to 10 mg of finely ground sample is further ground with a drop or two of mulling agent. These agents are substances that transmit a wide range of infrared frequencies and help minimize scattering by surrounding the analyte with a medium whose refractive index more closely matches that of the sample than does air. Nujol, refined mineral oil, is commonly

used although it is not appropriate for examination of aliphatic CH and CC vibrations. Several other materials are commonly used as well. The resulting mull should have a consistency resembling that of toothpaste. It is spread on a single plate of alkali halide or pressed between two such plates to adjust the thickness of sample.

Appendix C

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma (ICP) Discharge. The arc and spark sources date to the early development of emission spectroscopy in the mid-1800s; the inductively coupled plasma (ICP) discharge is a relatively recent development, and is among the most effective emission spectroscopic sources used today.

The ICP discharge is caused by the effect of a radio-frequency field on a flowing gas. In Fig.40 the discharge is induced without electrode contact in argon flowing upward through a quartz tube inside a copper coil or solenoid. The coil is energized by a radio-frequency generator operating between about 5 and 75 MHz; typical frequencies are 27 and 41 MHz. The radio-frequency signal creates a changing magnetic field H inside the coil in the flowing argon gas.

A changing magnetic field induces a circulating(eddy) current in a conductor, which in turn heats the conductor. At room temperature, argon is not a conductor, but it can be made

electrically conductive if heated. To start the ICP discharge, a pilot spark, arc, or Tesla discharge is applied to the argon. This pilot discharge absorbs energy from the changing magnetic field and turns rapidly into a stable discharge plasma that is thermally very hot and spectrally very intense. The equilibrium temperature in the annulus of an ICP discharge operating at 1 to 2 kW input power is about 9000 to 10,000 K.

More than one stream of argon is often used for spectrochemical analysis with the ICP discharge. One argon stream is confined to a volume near the tube walls to protect the quartz from the high-temperature discharge. A second argon stream carries the sample into the center of the discharge to produce an effective pathway through the discharge. If this pathway were not formed, the sample might flow around the hot discharge and be heated less effectively.

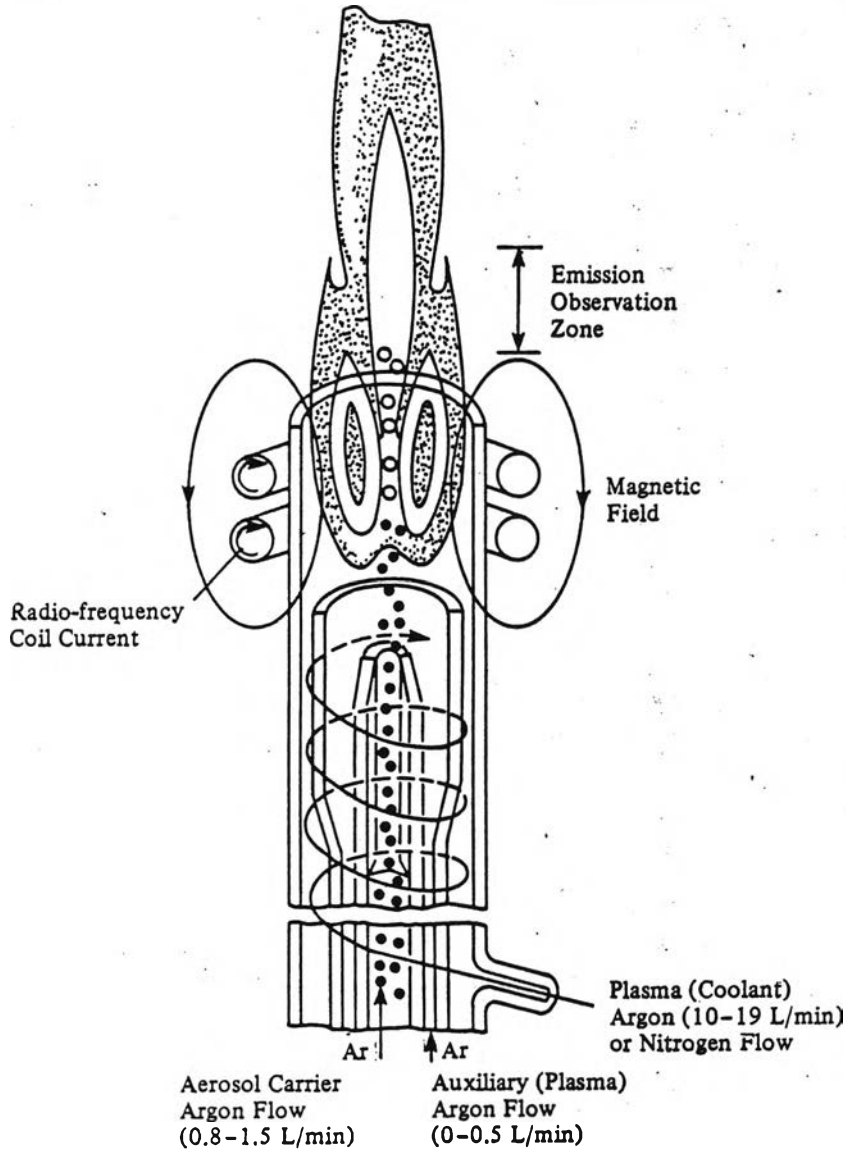


Fig.40 Schematic representation of an inductively coupled plasma discharge.(Christain and O'Reilly, 1986)

Although samples may be injected as powder, gases, or liquids, an arrangement similar to the spary chamber-nebulizer assembly used in flame spectroscopy is presently used. A complete nebulizer, spray chamber, and ICP discharge assembly is illustrated in Fig.41 , Although right-angle and concentric pneumatic nebulizer are widely applied for ICP emission spectroscopy , special-purpose nebulizers and ultrasonic nebulizers have been developed to enhance convenience or efficiency. The aerosol from the pneumatic nebulizer is transported by the central argon flow into the discharge directly, where the solvent is evaporated and analyte atomized. With ultrasonic nebulization, about 10 times more aerosol reaches the ICP, which could exceed the tolerance of the low-power discharge and cause it to be unstable. Thus, an oven is inserted between the ultrasonic nebulizer spray chamber and ICP discharge to remove the solvent before the aerosol enters the discharge . This arrangement increases the ICP sensitivity by 3 to 10 times.

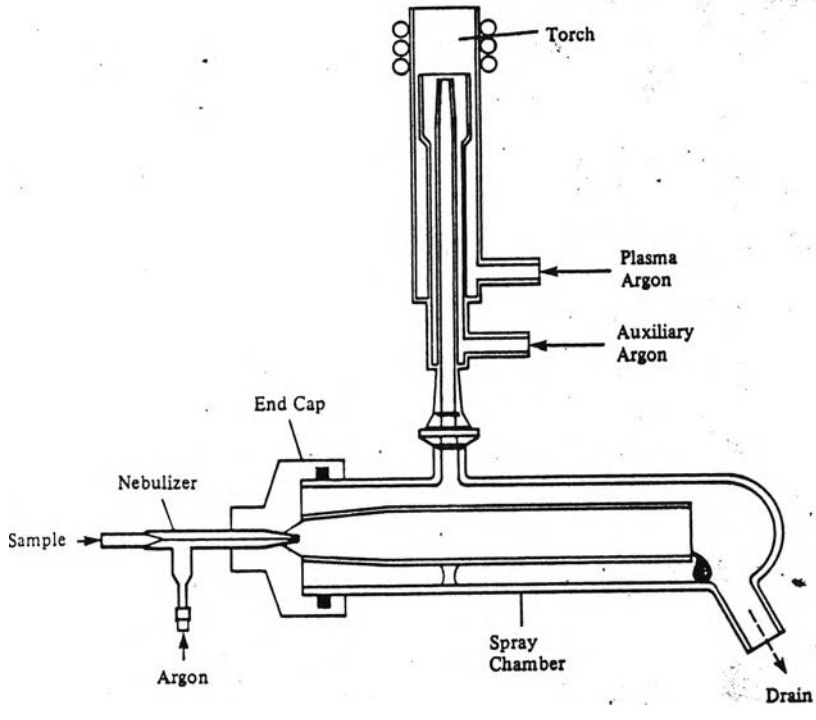


Fig.41 Concentric annular nebulizer, spray chamber, and torch apparatus for ICP emission spectroscopy. The sample is drawn into the nebulizer capillary by a controlled flow of argon through the outer jacket. Flow rate are typically 0.8 L/min argon and 1 mL/min analyte solution. The aerosol formed by the nebulizer is passed into a double spray chamber, where the larger droplets collect in the drain. About 2% of the original sample passes into the center tube of the ICP torch and into the ICP discharge. The same spray chamber can be adapted to a variety of nebulizers by replacing the end cap.

Because of the high temperatures available and the inert atmosphere of the ICP discharge, chemical interferences caused by the formation of stable compounds in flames are negligible with the ICP discharge, and thus releasing agents or special conditions are not needed. All compounds are likely to be atomized completely during their passage through the hot pathway in the center of the discharge. Ionization interferences that occur in excitation sources with high temperature such as the DC arc are minimal in the ICP plasma. For simultaneous mutielement analysis, such interference can generally be kept to less than 10% under coompromise analysis conditions.

All of properties of the ICP discharge provide excellent capabilities for quantitative analysis. Three operating parameters are crucial: input power, plasma gas flow rate, and observation height above the inductive coil. These operating conditions can be readily selected so that nearly optimum signal intensities for most elememts can be obtained in a single spectroscopic viewing region above the hot discharge. This allows the simultaneous determination of 35 elements, example, in a single sample without modifying the conditions for each element.

Appendix D

Instrumental Neutron Activation Analysis (INAA)

Activation analysis is a technique of elemental analysis based on selectively inducing radioactivity in some atoms of the elememts that make up the sample and then selectively measuring the radiations emitted by the radioactive atoms. Qualitative identification is achieved from the energy of the emitted spectrum. Quantitative determination is based on the intensity of radiation(s) characteristic of the particular element.

Neutron activation is the general term for irradiating material with neutrons to create radionuclides. Neutron activation analysis involves bombarding the sample with neutrons and measuring the radioactivity induced in the sample (commonly using gamma-ray spectrometry) . Neutrons are nuclear particles with unit mass number and neutral charge; they are commonly produced as a result nuclear reactions or nuclear fission, and interact with matter almost exclusively by collisions with nuclei. A neutron interacts with the

nucleus of an atom in several ways. It can undergo elastic scattering, whereby the neutron collides with the target nucleus and is scattered . Depending on the size of the target nucleus and the angle of collision , a varying amount of the kinetic energy of the neutron is lost in adding kinetic energy to the target nucleus. If the target nucleus has a low mass, a considerable fraction of the energy of the incident neutron may be lost in the collision . This is why low-mass materials are used to reduce the kinetic energy of fast neutrons produced by fission in nuclear reactors - a process known as thermalization.

A neutron also undergoes inelastic scattering with the target nucleus. In this case, the neutron scatters off the necleus of a target atom, transfers part of its kinetic energy, and excites the nucleus to one of its higher energy levels. The target nucleus can then dissipate this excess energy by emitting electromagnetic radiation

The third type of neutron interaction, the capture reaction , is the most important one of activation analysis. The coming neutron is absorbed (captured) by a target nucleus, forming a nuclide with the same atomic number as the parent nuclide, but one of unit higher in mass number. An amount of energy equal to the binding energy of the neutron in that

nucleus plus the kinetic energy of the incoming neutron is then avalible to raise the product nucleus to an excited state. The binding energy differs for different nuclides; but, for the most stable nuclides of intermediate mass , it is about 8MeV/neuteon. Thus, even if the capture neutron has almost zero kinetic energy, the excess energy of the compound nucleus is about 8 MeV.

There are two ways in which the compound nucleus can release thie excess energy: (a)It may radiate gamma rays, or (b) it may emit one or more nuclear particles (neutrons, protons, or alpha particles). Which of these two processes predominates depends on the total excitation energy the compound nucleus. If sufficient energy is available, more than one reaaction can take place.

To detect sample by INAA, the sample is exposed to neutrons for a known length of time then it is transported to counting station and allowed to cool or decay for a definite length of time. Gamma-ray spectrum is acquired for counting time, the area under the full-energy peak (FEP) of interest is calculated.

This procedure is repeated for another sample,(the standard) containing a known amount of the element of interest. From the weight of the element in the stsndard, the relative

FEP areas of the sample and atandard, the relative neutron fluxes used for irriadiating the sample and standard, and the times involved, the amount of the element in the sample is calculated.

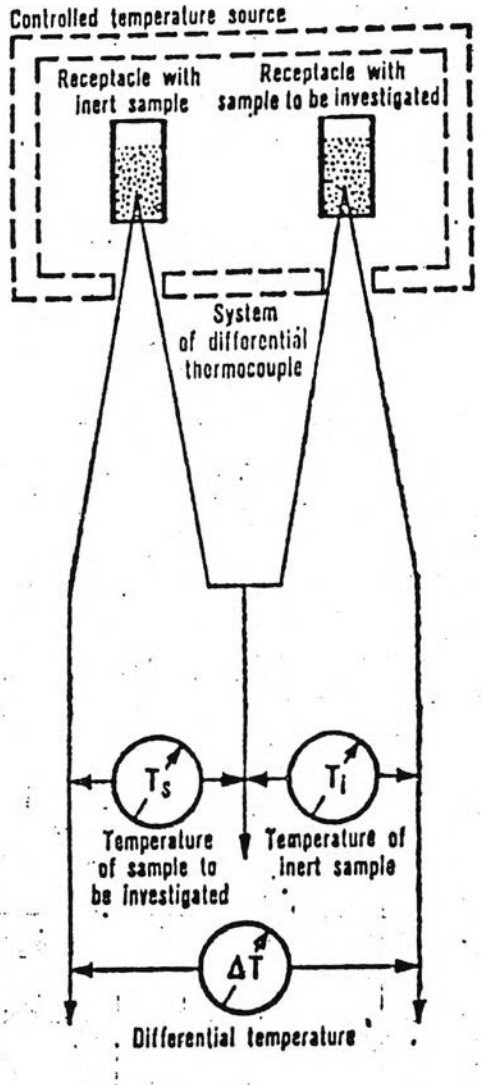
Appendix E

Differential Thermal Analysis (DTA)

Differential thermal analysis essential represents an instrumental modernization of the conventional method of investigating phase transformations by means of time(t) and temperature(T) recordings obtained during the uniform heating of a solid substance. Experimentally the method consists of heating under identical condions a sample and a thermally inert reference material while continually recording T existing in the furnace and the temperature difference ΔT resulting between the sample and the reference material. Under ideal conditions, the temperature difference ΔT which results in the course of heating or cooling should be recorded at a uniform rate proportional to the temperature of the sample or of the inert reference material or of the surrounding medium, depending on the type of instrument used.

These investigations are carried out with various types of instruments or differential calorimeters of furnace design whose rate of heating in time is constant. As a rule the temperature difference between the sample and the inert

material is recorded with a differential thermocouple device having one thermocouple placed in the sample and the other in the reference material, both being simultaneously heated at a constant rate (Fig.42)



ΔT; is the temperature difference between sample and inert thermal substance

T_s; is the temperature of the sample

T_i; is the temperature of the substance.

Fig.42 Schematic diagram of an apparatus for differential thermal analysis (Toder, 1976).

Assuming the temperature flow to be equivalent in the furnace, in the sample and in the inert substance, hence a temperature difference between them equal to zero , the instrument would then record the so-called *base line* as a function of time and temperature $\Delta T = 0$. If one phase is modified or if a decomposition reaction takes place in the sample with heat absorption or evolution, the temperature gradient against the reference material will then be modified and the temperature variation will be recorded by the instrument as an electromotive force deviating from the initial base line. The sense of the deviation against the zero line is determined by the temperature gradient between the sample and the reference material, showing at the same time the nature of the thermal process taking place. Hence, since the conversions occuring in the sample investigation involve enhermal or exothermal processes ,they may produce negative or positive deviations of the temperature difference ΔT against the arbitrary zero line ($\Delta T \neq 0$).

Such variations depend not only on the nature of the thermal process which takes place, but also on some physical properties of the material under investigation on the heating or cooling rate, and on some basic factors.

Any physical conversions or chemical reactions

generated by temperature hence produce a maximum in the recording of the temperature difference as a function of time $\Delta T = f(t)$; from this maximum it is possible to obtain information concerning the temperature and the conversion rate. Fig.43 illustrates schematically the diagram of a differrential thermal curve.

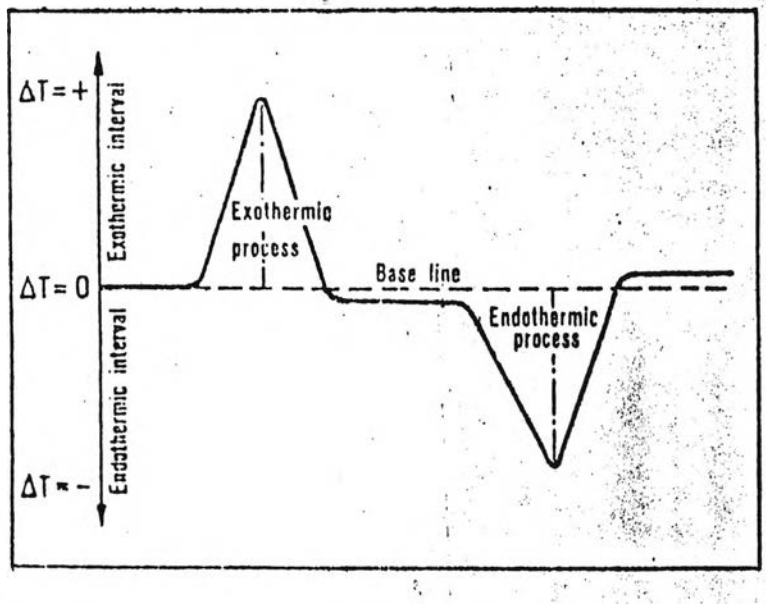


Fig.43 Idealized diagram of a DTA curve. (Todor, 1976)

To detect the DTA curve, 0.2500 grams of sample / 0.2500 grams of inert thermal substance (alumina) were ground into fine powders in porcelain motar and added in alumina receptacles in side of sample and inert thermal substance respectively. Temperature program was started from 20°C to 1350°C, heating rate 5°C/min.

Appendix F

X-Ray Diffraction Card of Hydroxyapatite

9-432 MAJOR CORRECTION

d	2.81	2.78	2.72	8.17
I/I$_1$	100	60	60	11

$Ca_5(PO_4)_3(OH)$ $1/2[Ca(OH)_2 \cdot 3Ca_3(PO_4)_2]$ ★

CALCIUM PHOSPHATE HYDROXIDE (HYDROXYL-APATITE)

Rad. CuKα$_1$ λ 1.5405 Filter Dia. 114.6mm
Cut off 50 I/I$_1$ PHOTOMETER* (GUINIER CAMERA)
Ref. DE WOLFF, TECHN. PHYS. DIENST, DELFT, HOLLAND

Sys. HEXAGONAL S.G. $P6_3/M$ (176)
a_o 9.418 b_o c_o 6.884 A C 0.7309
α β γ Z 2 Dx 3.16
Ref. IBID.

ε α ω γ Sign
2V D 3.08 mp Color
Ref.

* I-I$_1$ ARE PEAK VALUES FROM A PATTERN WHICH SHOWS SLIGHT BROADENING OF PRISM REFLECTIONS.
SAMPLE OBTAINED FOLLOWING THE PROCEDURE INDICATED BY HODGE C.S., IND. ENG. CHEM. ANAL. ED. 10 156 (1938).

d Å	I/I$_1$	hkl	d Å	I/I$_1$	hkl
8.17	12	100	2.040	2	400
5.26	6	101	2.000	6	203
4.72	4	110	1.943	30	222
4.07	10	200	1.890	16	312
3.88	10	111	1.871	6	320
3.51	2	201	1.841	40	213
3.44	40	002	1.806	20	321
3.17	12	102	1.780	12	410
3.08	12	210	1.754	16	402,303
2.814	100	211	1.722	20	004,411
2.778	60	112	1.684	4	104
2.720	40	300	1.644	10	322,223
2.631	25	202	1.611	8	313
2.528	6	301	1.587	4	501,204
2.296	8	212	1.542	6	420
2.262	20	310	1.530	6	331
2.228	2	221	1.503	10	214,421
2.148	10	311	1.474	12	502
2.134	4	302	1.465	4	510
2.065	8	113	PLUS ADDITIONAL LINES		

Appendix G

X-Ray Diffraction Card

of Monocalcium Phosphate Monohydrate

9-347 MAJOR CORRECTION

d	3.88	3.69	11.7	11.7	$Ca(H_2PO_4)_2 \cdot 1H_2O$
I/I_1	100	90	75	75	CALCIUM HYDROGEN ORTHOPHOSPHATE

Rad. $CuK\alpha_1$ λ 1.5405 Filter Dia. 114.6MM
Cut off 50 I/I_1 PHOTOMETER (GUINIER CAMERA)
Ref. DEWOLFF, TECHN. PHYS. DIENST, DELFT, HOLLAND

Sys. TRICLINIC S.G.
a_o 6.250 b_o 11.892 c_o 5.629 A 0.52556 C 0.47334
α 96.67° β 114.21° γ 92.56° Z 2 Dx 2.22
Ref. IBID.

εα 1.501 nωβ 1.518 εγ 1.528 Sign
2V D 2.220 mp Color
Ref. BALE, BONNER, HODGE, IND. ENG. CHEM., ANAL. ED. 17 491 (1945)

COMMERCIAL SAMPLE, RECRYSTALLIZED

d Å	I/I_1	hkl	d Å	I/I_1	hkl
11.7	75	010	2.952	30	111
5.85	10	020	2.935	10	040
5.66	16	100	2.833	12	200
5.34	2	$1\bar{1}0$	2.788	10	$11\bar{2}$
4.94	10	$01\bar{1}$,101	2.728	10	$1\bar{3}0$,041
4.90	20	110	2.688	14	210
4.65	4	$11\bar{1}$	2.677	6	$13\bar{1}$
4.42	16	011	2.669	25	$2\bar{2}0$
4.32	10	$1\bar{2}0$	2.652	4	$11\bar{2}$
4.16	14	$02\bar{1}$	2.640	2	$12\bar{2}$
3.88	100	$12\bar{1}$	2.585	12	$14\bar{1}$
3.69	90	$12\bar{1}$	2.560	20	$01\bar{2}$
3.58	14	021	2.537	2	002
3.40	6	$1\bar{3}0$	2.473	8	$13\bar{1}$,022
3.35	16	$03\bar{1}$	2.452	16	$23\bar{1}$,220
3.19	16	$1\bar{1}1$	2.428	8	$23\bar{0}$,$1\bar{2}2$
3.18	14	101	2.406	10	012,$13\bar{2}$
3.15	10	$13\bar{1}$	2.392	10	$23\bar{1}$,041
3.08	8	$20\bar{1}$	2.347	4	050,$14\bar{1}$
2.996	25	$12\bar{1}$,$13\bar{1}$	SEE FOLLOWING CARD		

9-347a MAJOR CORRECTION

d	3.88	3.69	11.7	11.7	$Ca(H_2PO_4)_2 \cdot 1H_2O$
I/I_1	100	90	75	75	CALCIUM HYDROGEN ORTHOPHOSPHATE HYDRATE

Rad. λ Filter Dia.
Cut off I/I_1
Ref.

Sys. S.G.
a_o b_o c_o A C
α β γ Z Dx
Ref.

εα nωβ εγ Sign
2V D mp Color
Ref.

SEE PRECEDING CARD

d Å	I/I_1	hkl	d Å	I/I_1	hkl
2.323	4	$22\bar{2}$	1.854	2	
2.296	4	131,$03\bar{2}$	1.845	4	
2.266	2	$05\bar{1}$	1.831	6	
2.240	4	$23\bar{2}$	1.792	12	
2.211	4	022	1.780	4	
2.158	8	$\bar{2}40$,$24\bar{1}$	1.762	8	
2.147	8	$14\bar{2}$	1.745	8	
2.124	6	201	1.722	4	
2.097	4	$24\bar{1}$	1.703	10	
2.081	10	$15\bar{1}$,$04\bar{2}$			
2.046	4	$1\bar{1}2$,$23\bar{2}$,$15\bar{1}$			
2.021	10	012			
1.996	20	032			
1.958	8	060,$30\bar{2}$			
1.942	12	$\bar{2}12$			
1.934	10	$11\bar{2}$,$31\bar{2}$,240			
1.925	8	$13\bar{2}$,061,$32\bar{1}$			
1.881	2				
1.872	4				
1.863	2				

Appendix H

X-Ray Diffraction Card

of Dicalcium Phosphate Dihydrate

9-77 MAJOR CORRECTION

d	7.57	4.24	3.05	7.57
I/I$_1$	100	100	75	100

$CaHPO_4 \cdot 2H_2O$

CALCIUM HYDROGEN ORTHOPHOSPHATE HYDRATE (BRUSHITE)

Rad. $CuK\alpha_1$ λ 1.5405 Filter Dia. 114.6MM
Cut off 50 I/I$_1$ PHOTOMETER (GUINIER CAMERA)
Ref. DEWOLFF, TECHN. PHYS. DIENST, DELFT, HOLLAND

Sys. MONOCLINIC S.G. C_2 (5)
a_o 6.363 b_o 15.19 c_o 5.815 A 0.4189 C 0.3828
α β 118.48° γ Z 4 Dx 2.32
Ref. IBID.

$\varepsilon\alpha$ 1.540 $n\omega\beta$ 1.545 $\varepsilon\gamma$ 1.555 Sign −
2V D 2.306 mp Color
Ref. BALE, BONNER, HODGE, IND. ENG. CHEM., ANAL. ED., 17 491 (1945)

BEEVERS ACTA CRYST 11 273-277 (1958) GIVES A = 5.812, B = 15.180, C = 6.239, β = 116 25. S.G. I2/A A = 6.359, B = 15.180, C = 5.188, β = 118 31 S.G. C_2/c IN THE SETTING USED HERE.

d Å	I/I$_1$	hkl	d Å	I/I$_1$	hkl
7.57	100	020	2.252	2	240
4.93	2	11$\bar{1}$	2.172	20	151
4.24	100	021	2.148	16	24$\bar{2}$
3.80	8	040	2.120	2	042
3.75	< 1	130	2.100	6	15$\bar{2}$
3.63	2	13$\bar{1}$	2.084	10	31$\bar{1}$
3.05	75	111,041	2.022	4	170,31$\bar{2}$
2.928	50	22$\bar{1}$	2.001	10	221,17$\bar{1}$
2.855	10	11$\bar{2}$	1.976	6	26$\bar{1}$,112
2.797	2	200	1.943	2	331
2.670	4	150	1.899	2	000
2.648	4	131	1.888	4	11$\bar{3}$
2.623	50	220,15$\bar{1}$	1.878	14	260
2.603	30	20$\bar{2}$	1.858	d	22$\bar{3}$
2.554	4	002	1.855	< 1	132
2.532	2	060	1.819	20	241
2.520	4	13$\bar{2}$	1.799	10	062
2.434	14	24$\bar{1}$	1.780	4	081,171+
2.421	16	022	1.748	2	330
2.268	4	061	PLUS ADDITIONAL LINES		

Appendix I

X-Ray Diffraction Card of β-Tricalcium Phosphate

Beta Tricalcium Phosphate

(β - $Ca_3(PO_4)_6$)

Indices (hkl)	d(A°)	I/I_o	Indices (hkl)	d(A°)	I/I_o
012	8.15	12	220	2.607	65
104	6.49	16	0.1.14	2.562	6
006	6.22.	6	223	2.553	8
110	5.21	20	2.1.10	2.520	12
113	4.80	2	131	2.499	6
202	4.39	8	1.2.11, 226	2.407	10
018	4.15	4	315	2.375	6
024	4.06	16	1.0.16	2.263	10
116	4.00	4	1.1.15	2.249	4
1.0.10	3.45	25	042	2.241	2
211	3.40	4	404	2.195	14
122	3.36	10	3.0.12	2.165	12
199, 208	3.25	8	1.2.14	2.103	4
214	3.21	55	0.2.16+	2.076	8
0.0.12, 125	3.11	2	321	2.063	4
300	3.01	16	232	2.061	6
0.2.10, 217	2.880	100	048	2.033	10
128	2.757	20	324	2.023	6
306	2.710	10	3.1.11	2.017	4
1.1.12	2.674	8	Plus Additional lines		

Appendix J

X-Ray Diffraction Card

of α-Tricalcium Phosphate

9-348 MAJOR CORRECTION

d	2.91	2.62	3.91	12.3	α-$Ca_3(PO_4)_2$
I/I_1	100	50	40	4	ALPHA CALCIUM ORTHOPHOSPHATE

Rad. $CuK\alpha_1$ λ 1.5405 Filter Dia. 114.6mm
Cut off 50 I/I_1 PHOTOMETER (GUINIER CAMERA)
Ref. DEWOLFF, TECHN. PHYS. DIENST, DELFT, HOLLAND

Sys. ORTHORHOMBIC* S.G.
a_o 15.22 b_o 20.71 c_o 9.109 A 0.7349 C 0.4398
α β γ Z 16 Dx 2.87
Ref. IBID.

ε α nωβ β γ Sign
2V D 2.814 mp 1720°C Color
Ref. MACKAY (SEE BELOW)

* STATED TO BE MONOCLINIC PSEUDORHOMBIC BY MACKAY, ACTA CRYST. 6 743 (1953)
SAMPLE OBTAINED BY HEATING β-PHASE AT 1400°C.

d Å	I/I_1	hkl	d Å	I/I_1	hkl
12.3	4	110	3.35	8	312
7.31	25	111	3.33	4	421
6.82	4	021	3.15	4	260
6.29	10	130	3.12	4	242
6.12	4	220	3.07	4	440
5.83	10	201	3.05	4	332
5.18	12	131,040	3.01	20	510
4.55	4	002	2.947	20	113
4.33	4	311	2.919	35	402,023
4.28	2	240,112	2.905	100	441,170
4.17	2	022	2.860	30	511
4.00	20	150	2.816	2	203,422
3.91	40	202	2.786	12	530
3.88	40	241	2.767	4	171
3.81	8	400	2.734	< 1	133
3.73	4	331	2.720	< 1	223
3.69	40	132	2.665	4	531
3.66	18	151,222	2.621	50	043,352
3.51	4	401	2.590	30	080
3.45	6	060	PLUS ADDITIONAL LINES		

Appendix K

American Standard Test Methods for Composition of Ceramic Hydroxyapatite for Surgical Implants

Designation: F 1185 – 88

Standard Specification for Composition of Ceramic Hydroxylapatite for Surgical Implants[1]

This standard is issued under the fixed designation F 1185; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This specification covers material requirements for ceramic hydroxylapatite intended for surgical implants. For a material to be called ceramic hydroxylapatite, it must conform to this specification. (See Appendix X1.)

1.2 The biological response to ceramic hydroxylapatite in soft tissue and bone has been characterized by a history of clinical use (1, 2, 3)[2] and by laboratory studies (4, 5, 6).

1.3 This specification specifically excludes hydroxylapatite coatings, non-ceramic hydroxylapatite, ceramic-glasses, tribasic calcium phosphate, whitlockite, and alpha- and beta-tricalcium phosphate. (See Specification F 1088.)

2. Referenced Documents

2.1 *ASTM Standard:*
F 1088 Specification for Beta-Tricalcium Phosphate for Surgical Implantation[3]
2.2 *Code of Federal Regulations:*[4]
Title 21, Part 820.
2.3 *National Formulary:*[5]
Tribasic Calcium Phosphate
2.4 *United States Pharmacopeia:*[6]
Identification Tests for Calcium and Phosphate <191>
Lead <251>
Mercury <261>
Arsenic <211>
Heavy Metals <231> Method 1
2.5 *U. S. Geological Survey Method:*[7]
Cadmium

3. Descriptions of Terms Specific to This Standard

3.1 *hydroxylapatite*—the chemical substance having the empirical formula $Ca_5(PO_4)_3OH$.[8]

3.2 *ceramic hydroxylapatite*—hydroxylapatite which has been fired at sintering temperatures. Firing time is mass dependent, and should be sufficiently long to cause significant densification and formation of a biologically stable form.

3.3 *sintering*—an integration of time and temperature of a ceramic precursor which develops a coherent body with useful properties. Sintering is a non-melting process accompanied by significant surface area and bulk volume reductions (densification), grain growth, and increases in mechanical properties.

3.4 *calcining*—the heat treatment of a ceramic precursor for the purpose of eliminating volatile constituents. Calcining is also accompanied by some surface area and bulk volume reductions. Increases in mechanical properties are not usually significant.

4. Chemical Requirements

4.1 Elemental analysis for calcium and phosphorus will be consistent with the expected stoichiometry of hydroxylapatite.

4.2 A quantitative X-ray diffraction analysis shall indicate a minimum hydroxylapatite content of 95 % (7). Analysis of relative peak intensities shall be consistent with published data.[9]

4.3 The concentration of trace elements in the hydroxylapatite shall be limited as follows:

Element	ppm, max
As	3
Cd	5
Hg	5
Pb	30
total heavy metals (as lead)	50

For referee purposes, methods in 2.4 and 2.5 shall be used.

4.4 The maximum allowable limit of all heavy metals determined as lead will be 50 ppm as described in 2.4 or equivalent. Sample preparation will be identical to that for tribasic calcium phosphate as specified in the National Formulary (2.2) except that approximately 1 g of material will be dissolved in approximately 30 mL of 5 % HCl and boiled.

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[1] This specification is under the jurisdiction of ASTM Committee F-4 on Medical and Surgical Materials and Devices and is the direct responsibility of Subcommittee F04.02 on Resources.
Current edition approved Oct. 31, 1986. Published December 1988.

[2] The boldface numbers in parentheses refer to the list of references at the end of this specification.

[3] *Annual Book of ASTM Standards*, Vol 13.01.

[4] Available from U.S. Government Printing Office, Washington, DC 20402.

[5] National Formulary XVI. Available from U.S. Pharmacopeia Convention, Inc., 12601 Twinbrook Parkway, Rockville, MD 20852.

[6] United States Pharmacopeia XXI. Available from U.S. Pharmacopeia Convention, Inc., 12601 Twinbrook Parkway, Rockville, MD 20852.

[7] Crock, J. G., Felichte, F. E., and Briggs, P. H., "Determination of Elements in National Bureau of Standards Geological Reference Materials SRM 278 Obsidian and SRM 688 Basalt by Inductively Coupled Argon Plasma—Atomic Emission Spectrometry," *Geostandards Newsletter*, Vol 7, 1983, pp. 335-340.

[8] Chemical Abstracts Service Registry Number [1306-06-5].

[9] The Joint Committee on Powdered Diffraction Standards has established a Powder Diffraction File. The Committee operates on an international basis and cooperates closely with the Data Commission of the International Union of Crystallography and ASTM (American Society for Testing and Materials). Hydroxylapatite data can be found on file card number 9-432 and is available from the Joint Committee on Powder Diffraction Standards, 1600 Park Lane, Swarthmore, PA 19081.

4.5 It is recommended that all metals or oxides not detected as lead present in concentrations equal to or greater than 0.1 % be listed on the package insert.

5. Test Specimen Fabrication

5.1 Prepare test specimens from the same batch of material and by the same processes as those employed in fabricating the ceramic implant device.

6. Quality Program Requirements

6.1 The manufacturer shall conform to Good Manufacturing Practices (2.2) or its equivalent.

APPENDIX

(Nonmandatory Information)

X1. RATIONALE

X1.1 Ceramic hydroxylapatite is commercially available as a synthetic bone-grafting material. As with any implant material, the bioresponse is critically dependent upon the material properties. To achieve reliable biocompatibility these must be known and consistent. This material standard provides specifications for a biocompatible grade of hydroxylapatite. Trace element content and leachability, physical form, and size must be within established biocompatibility standards.

X1.2 X-ray powder diffraction analysis provides better differentiation between hydroxylapatite and several commonly occurring second phases than traditional wet chemical methods.

X1.3 It is recognized that a separate performance standard may be necessary for each end-use product. For this reason, physical and mechanical properties were not specified. A source of general test methods for ceramics may be found in Ref (8).

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(3) Yukna, R. A., Mayer, E. T., Brite, D. V., "Longitudinal Evaluation of Durapatite Ceramic as an Alloplastic Implant in Periodontal Osseous Defects After Three Years," *Journal of Periodontology*, Vol 55 (11), 1984, pp. 633-637.

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(5) Drobeck, H. P., Rothstein, S. S., Gumaer, K. I., Sherer, A. D., and Slighter, R. G., "Histologic Observation of Soft Tissue Responses to Implanted, Multifaceted Particles and Discs of Hydroxylapatite," *Journal of Oral and Maxillofacial Surgery*, Vol 42, 1984, pp. 143-149.

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(8) *Annual Book of ASTM Standards*, Vol 15.02.

Vita

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