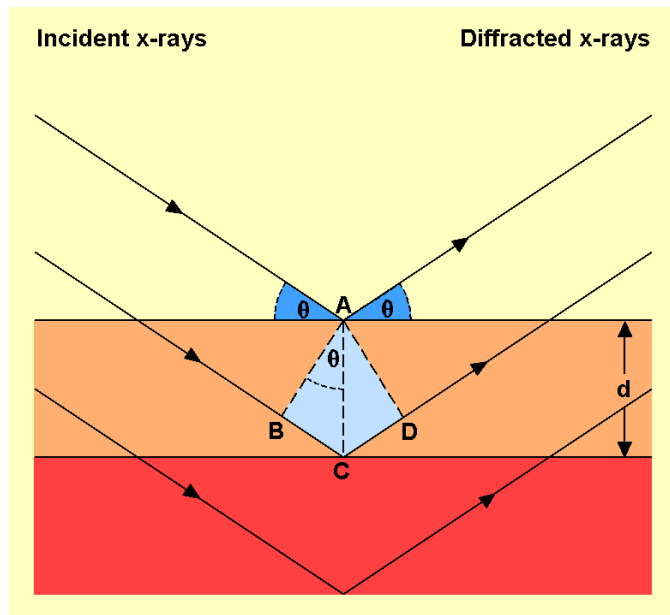


**CHEM.3040 – FORENSIC SCIENCE II**  
**FORENSIC APPLICATIONS OF X-RAY**  
**DIFFRACTION**

### I. Introduction

Our knowledge of the crystalline state is gained by studies utilizing x-rays (the field of x-ray crystallography). Let us suppose that a beam of monochromatic x-rays is incident on a crystal (Fig. 1). If the wavelength of the x-rays is similar to that of the spacing between the planes of atoms (for example, let us assume we are using Cu K $\alpha$  radiation for which  $\lambda = 1.54 \text{ \AA}$ , an  $\text{\AA} = 1 \times 10^{-10} \text{ m}$ , a very small unit of distance) the x-rays will be scattered by the atoms. For certain incident angles and spacings between the planes of atoms constructive interference will occur and a diffracted beam will leave the crystal at an angle equal to that of the incident beam. The relationship between x-ray wavelength, angle of incidence and spacing between planes of atoms is known as Bragg's Law.

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



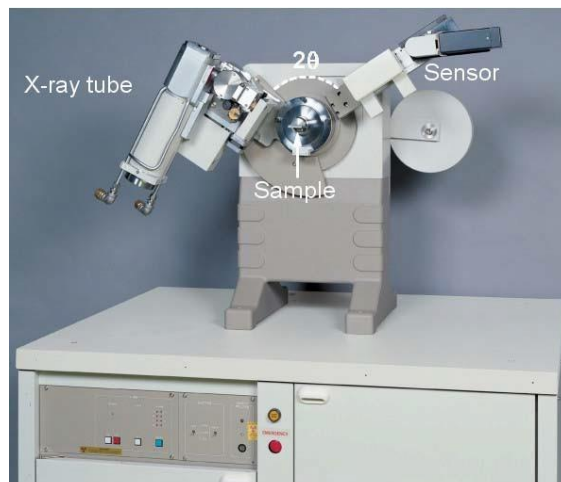
**Fig. 1.** Interaction between x-rays and the crystal structure.

Where  $\lambda$  is the x-ray wavelength,  $d$  is the spacing between planes of atoms, and  $\theta$  is the incident angle.

While a very simple equation, this relationship represents a powerful way to investigate the structure of crystalline materials. X-ray data for crystalline materials is often acquired using x-ray powder diffractometry (Fig. 2). An x-ray tube provides a monochromatic x-ray beam. Thus, the wavelength is known. The sample is in a fixed geometry, usually powder on a glass slide, and a sensor is scanned through a  $2\theta$  angle (Fig. 3). When constructive interference occurs a diffracted beam is sent to the sensor giving the  $2\theta$  angle. The remaining unknown is the  $d$  spacing. For any particular mineral there are multiple paths with different  $d$  spacings, and each of these will be recorded. In addition, for a mineral that consists of more than one element, the areal distribution of the different elements will vary as a function of the plane that is diffracting the x-ray beam. Since different atoms interact differently with the x-ray beam, the intensity of the diffracted signal varies as a function of the particular atomic plane that is responsible for the diffracted beam. Thus, we obtain a second important piece of information, the intensity of the diffracted x-ray beam, which can be related to the composition of the crystalline solid. Tens of thousands of crystalline compounds have been characterized by x-ray diffraction. Taking into account the  $d$ -spacing and relative intensities of the diffracted beam virtually every crystalline compound has a unique x-ray fingerprint. This information is available in the American Society for Testing and Materials Powder Data File which is frequently updated and contains information for



**Figure 2.** X-ray diffractometer.



**Figure 3.** Close-up view of x-ray tube, sensor, and sample (powder on glass slide).  $2\theta$  is the angle between the x-ray tube and the sensor.

all known crystalline materials. Thus, we have a powerful angle between the x-ray tube and the sensor. method for identifying crystalline solids even if individual particles are very small.

What we usually measure is the  $2\theta$  angle from which we can calculate the  $d$  spacing by solving Bragg's equation for  $d$ .

$$d = \frac{\lambda}{2 \sin\theta}$$

In the following problems we will be using a copper (Cu) x-ray tube in which case Bragg's law is

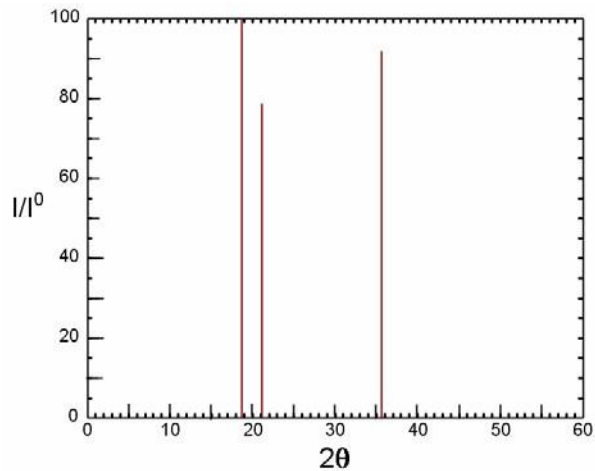
$$d = \frac{1.54\text{\AA}}{2 \sin\theta}$$

**Note that the diffraction angle is measured as  $2\theta$ . In the equation above we use the  $\theta$  angle. Hence, the  $2\theta$  angle must be divided by 2 to get the  $\theta$  angle used in the equation. For example, if the  $2\theta$  angle is  $32^\circ$ , the  $\theta$  angle is  $16^\circ$ .**

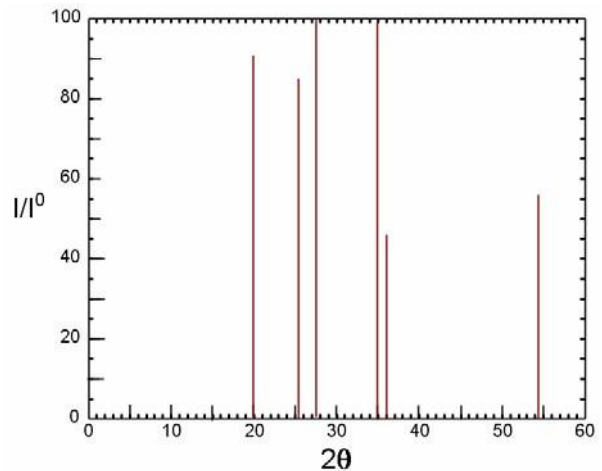
Reference x-ray diffraction patterns for a number of crystalline solids are attached to this exercise. These data are to be used in answering (solving) the following problems and cases. For the unknown XRD patterns only the three most intense peaks are shown for each crystalline solid in the unknown.

## II. Cosmetics

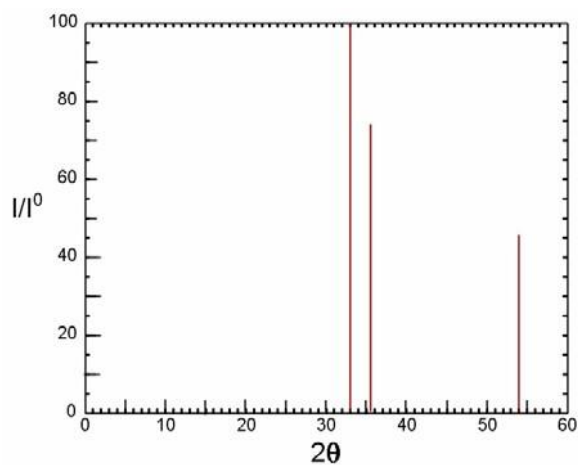
Various minerals are used in cosmetics to provide color and texture. In this exercise we will look at several types of lipsticks for which we have x-ray diffraction data. X-ray diffraction data for 4 lipsticks are shown below.



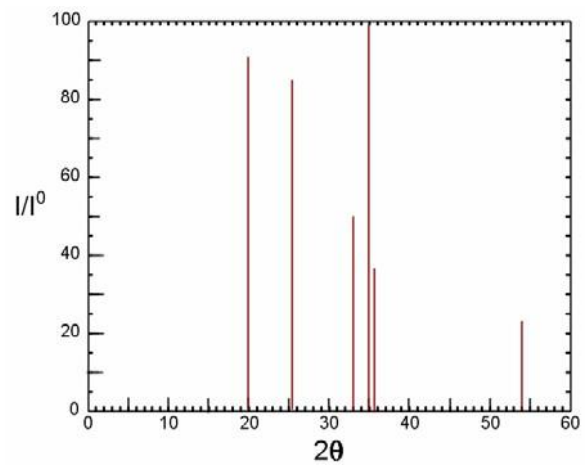
**Figure 4.** XRD pattern for Tropez A.



**Figure 5.** XRD pattern for Tropez B.



**Figure 6.** XRD pattern for Avon Red K.



**Figure 7.** XRD pattern for Cover Girl Classic Red

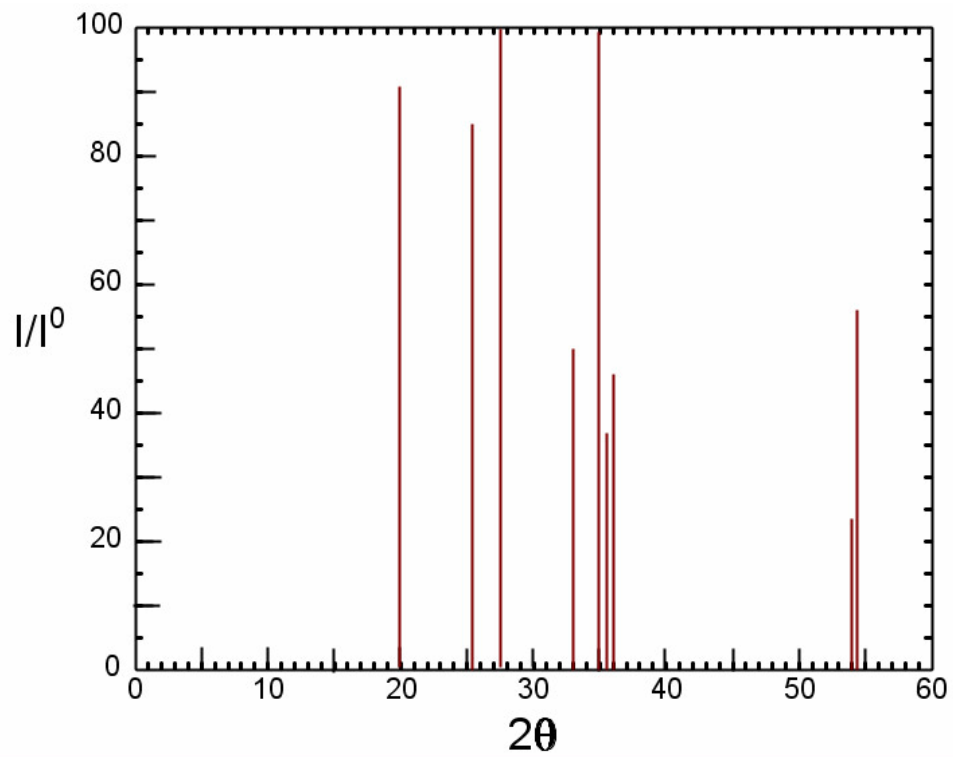
1. For Tropez A (Fig. 4) list the 2 theta angle, relative intensity, and d-spacing for each peak.

$2\theta$	$I/I_0$	$d$ (Å)

2. Does Tropez A (Fig. 4) contain either chlorite or kaolinite. How did you make this determination?

4. Identify the minerals in Avon Red K and Cover Girl Classic Red. If they contain mineral(s) in common, what role might these mineral(s) play in the appearance of the lipsticks?

[illegible]



**Figure 8.** XRD pattern for lipstick smear recovered from victim.

From this evidence, what can you conclude about possibility of either suspect being the murderer? Explain in detail?

### III. Pottery and Minerals

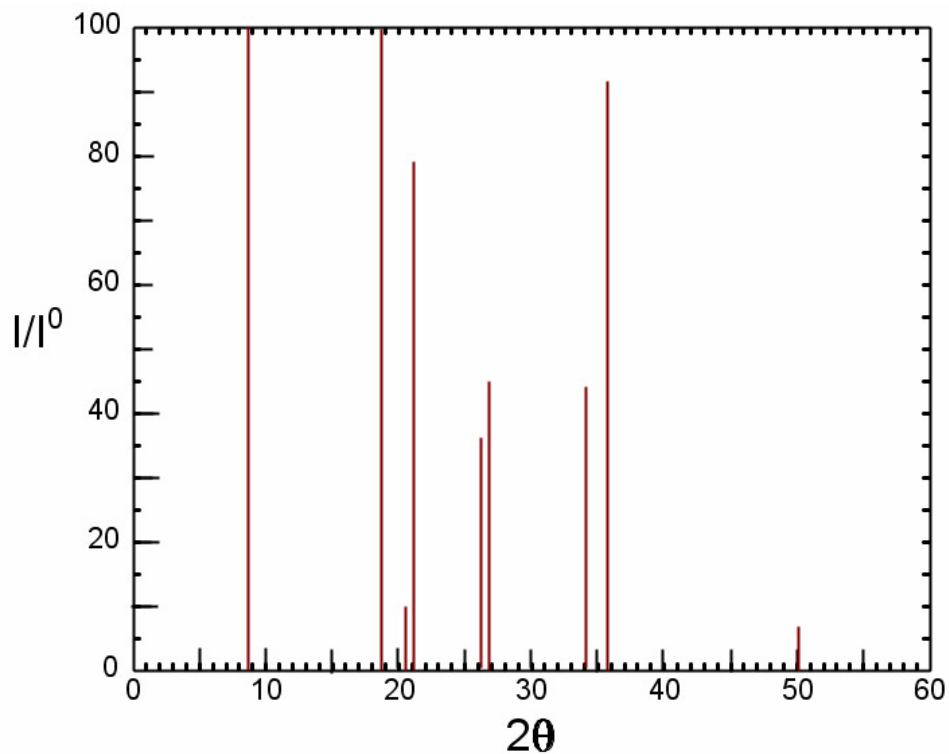
Minerals are used in pottery for the clay and glazes. Glazes are applied prior to firing of the pottery and provide the coloration. Given that any particular type of pottery may consist of a relatively unique group of minerals it is possible to characterize pottery from different sources. Pottery clays consists of mixtures of the following minerals - biotite, chlorite, kaolinite, kyanite, montmorillonite, pyrophyllite, and quartz. Different mixtures of minerals are used depending on the desired properties of the resulting pottery (ceramic). Minerals in the glazes are responsible for the final color of the pottery (Table 1).

Table 1. Minerals used for pottery glazes

Mineral	Formula	Color
Cassiterite	$\text{SnO}_2$	white
Cuprite	$\text{Cu}_2\text{O}$	green (oxidation), red (reduction)
Eskolaite	$\text{Cr}_2\text{O}_3$	green
Goethite	$\text{FeO}(\text{OH})$	yellow, tan, brown
Hematite	$\text{Fe}_2\text{O}_3$	tan, brown
Ilmenite	$\text{Fe}(\text{Ti,Mg})\text{O}_3$	tans and buffs
Pyrolusite	$\text{MnO}_2$	red, blue, purple, black
Rutile	$\text{TiO}_2$	yellow to tan (oxidation), blue and purple (reduction)
Sphaerocobaltite	$\text{CoCO}_3$	blue
Tenorite	$\text{CuO}$	green (oxidation), red (reduction)
Zincite	$\text{ZnO}$	brown

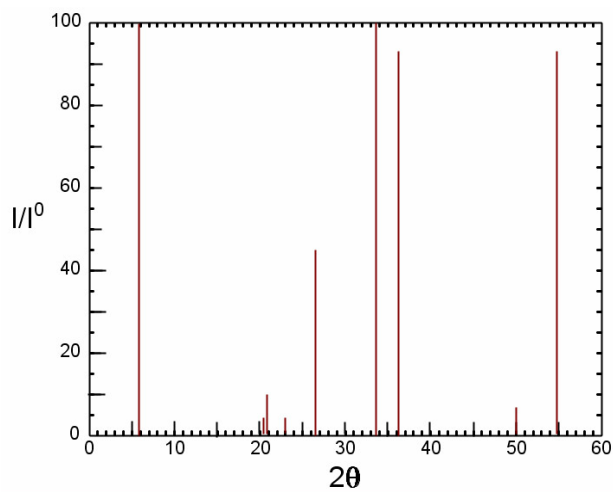
6. A piece of broken pottery is found at a crime scene. The XRD pattern for this pottery is shown on the next page (Fig. 9). Identify the minerals in the pottery. To do this you need to determine the two theta values and relative intensities. List the minerals and the pertinent data below.

2 $\theta$	$I/I_0$	Mineral

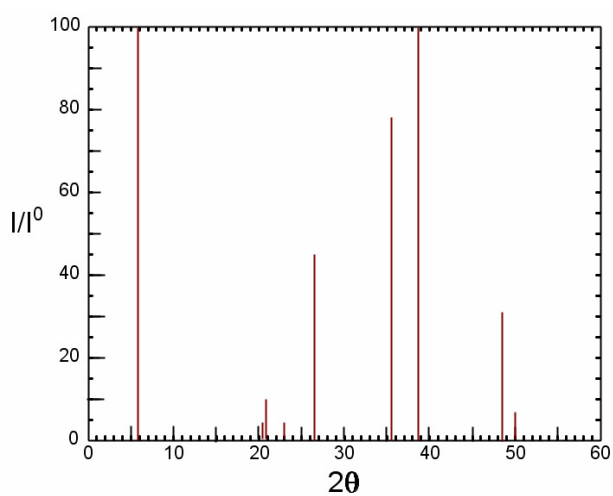


**Figure 9.** XRD pattern for broken pottery found at crime scene.

7. A piece of broken green pottery is found at a crime scene. A person of interest is apprehended and is found to have small bits of green pottery embedded in his shoe. The x-ray patterns for the crime scene (Fig. 10) and the pottery embedded in the shoe (Fig. 11) are shown below.



**Figure 10.** XRD pattern for broken pottery at crime scene.

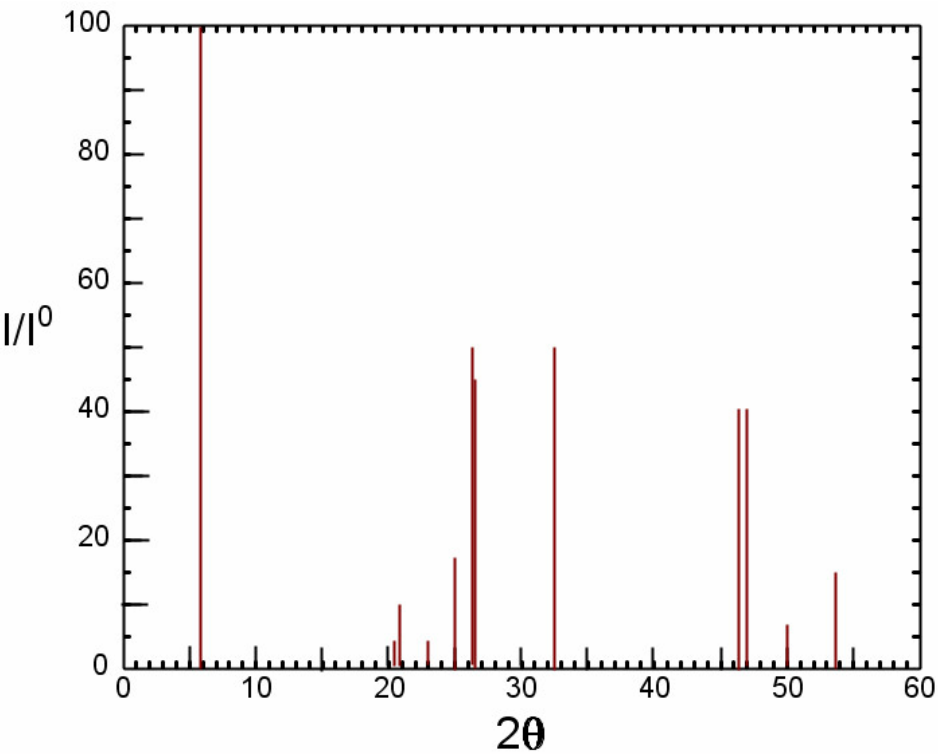


**Figure 11.** XRD pattern for piece of pottery embedded in suspect's shoe.

Identify the minerals in each pottery sample. Are there any differences? Explain. Is the pottery embedded in the suspect’s shoe from the crime scene? Explain.

Fig. 10				Fig. 11		
2θ	I/I <sub>0</sub>	Mineral		2θ	I/I <sub>0</sub>	Mineral

8. A nondescript powder is found adhering to a suspect’s pants leg. The XRD pattern for this unknown material is shown below (Fig. 12).



**Figure 12.** XRD pattern for powder on suspect’s pants.



Identify the minerals in the powder. List the minerals and the relevant x-ray data. What is the source of this powder? What was the most likely color of the object that was the source of the powder? Explain.

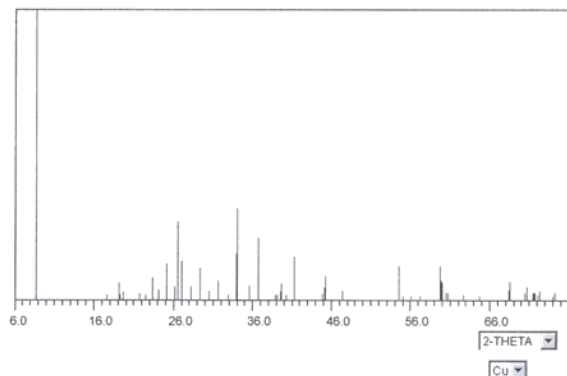
2θ	I/I <sub>0</sub>	Mineral

## XRD REFERENCE SPECTRA

All spectra are for Cu-K $\alpha$  x-rays ( $\lambda = 1.54\text{\AA}$ ).  $\text{\AA}$  = Angstrom, a unit of distance =  $1 \times 10^{-10}$  m.  $I/I^0$  is the relative intensity.  $I/I^0 = 100$  identifies the diffracted peak with the greatest intensity. The y-axis on each of the images is the relative intensity ( $I/I^0$ ). The line that extends to the top of the graph represents the peak with the greatest intensity. Using Bragg's Law, fill in the missing values in the tables. The X-ray spectra and data reported in the following figures and tables are from the site "<http://database.iem.ac.ru/mincryst/>".

### CLAYS IN POTTERY

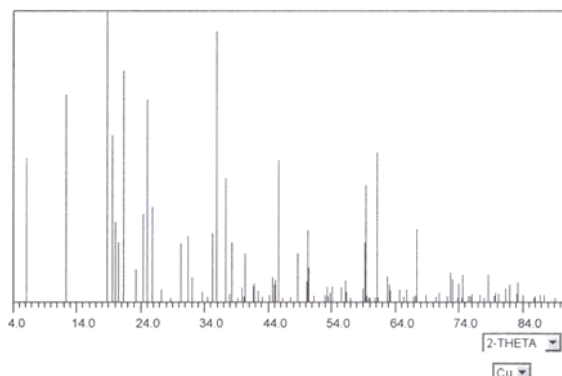
**BIOTITE, [3], 2M(1),  $K(\text{Mg,Fe})_3\{\text{AlSi}_3\text{O}_{10}\}(\text{OH})_2$**



Biotite

d	$I/I^0$	$\theta$	$2\theta$
10.064	100		
2.624	44		
3.401	36		

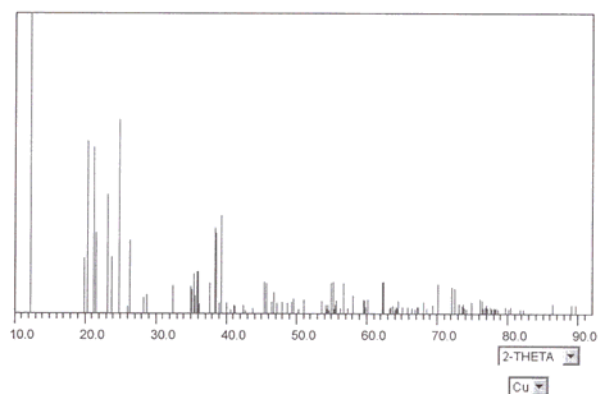
**CHLORITE, [1],  $\text{Al}_{2.0}[\text{Si}_{3.3}\text{Al}_{0.7}]\text{O}_{10}(\text{OH})_2[\text{Mg}_{2.3}\text{Al}_{0.7}](\text{OH})_6$**



Chlorite

d	$I/I^0$	$\theta$	$2\theta$
	100	9.4	18.8
	92	17.9	35.8
	79	10.6	21.3

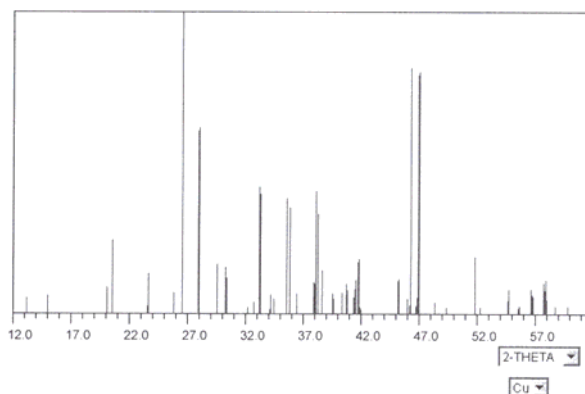
KAOLINITE, [2],  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$



Kaolinite

d	I/I°	$\theta$	2 $\theta$
	100	5.0	10.0
	12	8.2	16.3
	9	9.5	19.1

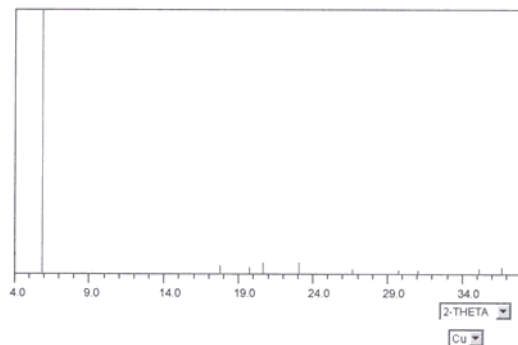
KYANITE, [1], structure type - kyanite,  $\text{Al}_2[\text{SiO}_5]$



Kyanite

d	I/I°	$\theta$	2 $\theta$
3.345	100		
1.957	81		
1.929	80		

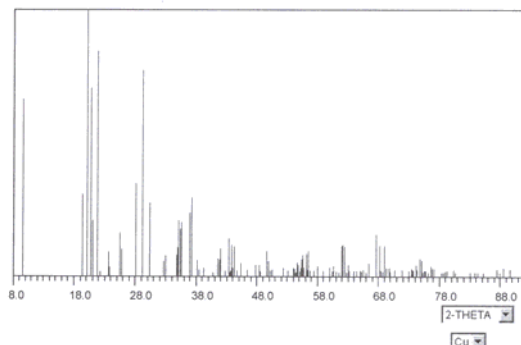
MONTMORILLONITE, [1], Ca, syn, DE,  $\text{Ca}_{0.5}\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$



Montmorillonite

d	I/I°	$\theta$	2 $\theta$
15.000	100	2.9	5.8
4.299	4	10.3	20.6
3.851	4	11.5	23.0

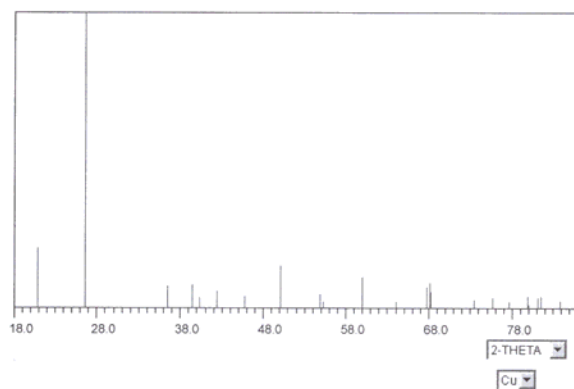
PYROPHYLLITE, [1], ITC,  $\text{Al}[\text{Si}_2\text{O}_5](\text{OH})$



Pyrophyllite

d	I/I°	$\theta$	2 $\theta$
4.411	100	10.1	20.1
4.060	84	10.9	21.8
3.061	77	14.6	29.0

**QUARTZ, [1], alpha, structure type - alpha-quartz, SiO<sub>2</sub>**

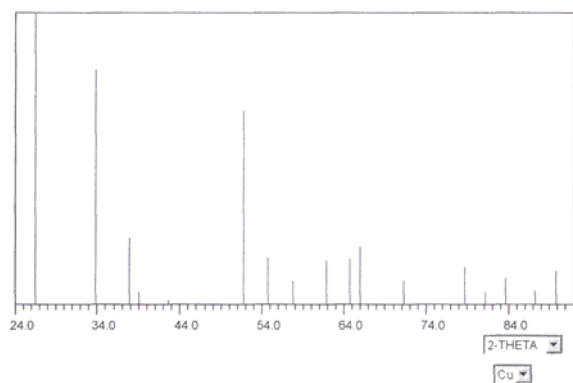


Quartz

d	I/I°	θ	2θ
3.344	100	13.3	26.6
4.256	20	10.4	20.8
1.818	14	25.1	50.1

**POTTERY  
GLAZES**

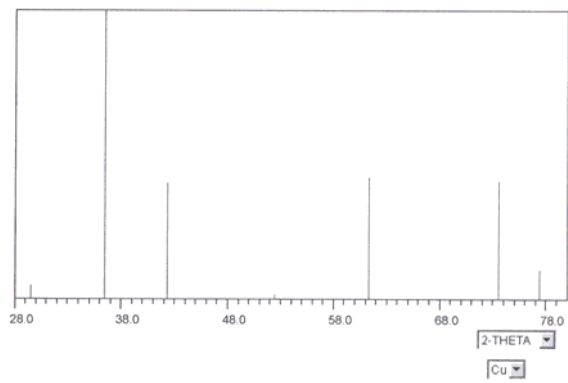
**CASSITERITE, [1], structure type - rutile, SnO<sub>2</sub>**



Cassiterite

d	I/I°	θ	2θ
3.350	100	13.3	26.6
2.644	80	16.9	33.8
1.764	66	25.9	51.8

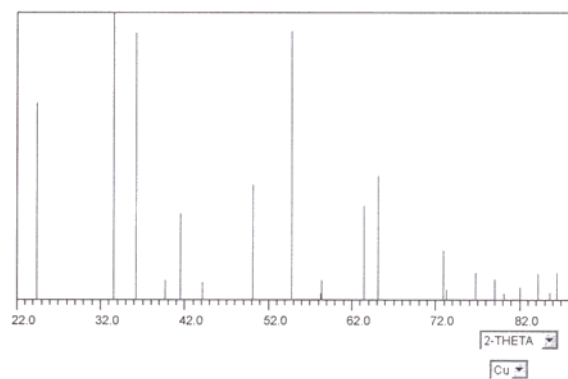
**CUPRITE, [1], structure type - cuprite, Cu<sub>2</sub>O**



Cuprite

d	I/I°	θ	2θ
2.465	100	18.2	36.4
1.510	41	30.7	61.3
1.287	41	36.7	73.5

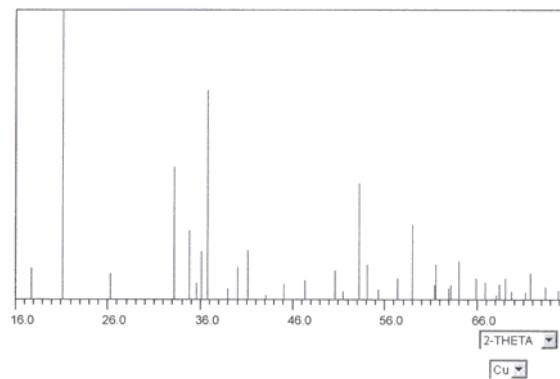
ESKOLAITE, [1], structure type - corundum,  $\text{Cr}_2\text{O}_3$



Eskolaite

d	I/I°	$\theta$	2 $\theta$
2.666	100	16.8	33.6
1.673	93	27.4	54.8
2.480	93	18.1	36.2

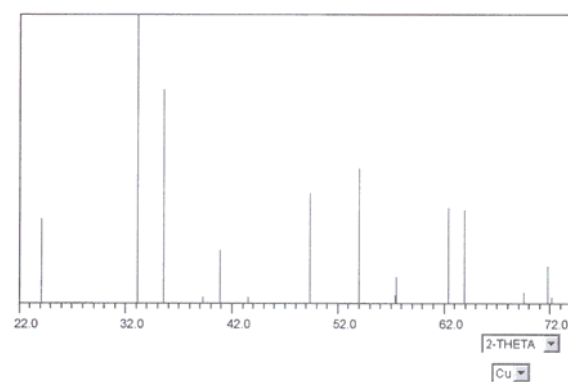
GOETHITE, [1], alpha, structure type - diaspor,  $\text{FeO}(\text{OH})$



Goethite

d	I/I°	$\theta$	2 $\theta$
4.190	100	10.6	21.2
2.445	72	18.4	36.7
2.694	45	16.6	33.2

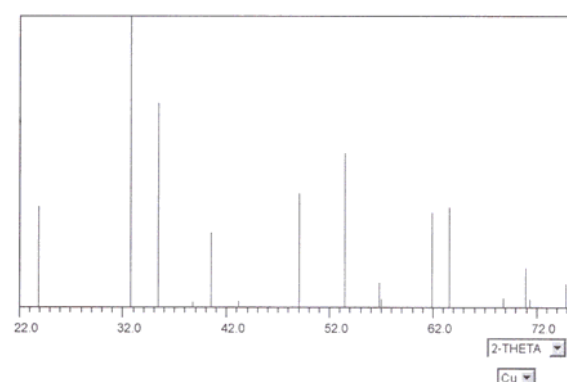
HEMATITE, [1], structure type - corundum,  $\text{Fe}_2\text{O}_3$



Hematite

d	I/I°	$\theta$	2 $\theta$
2.703	100	16.6	33.1
2.519	74	17.8	35.6
1.697	46	27.0	54.0

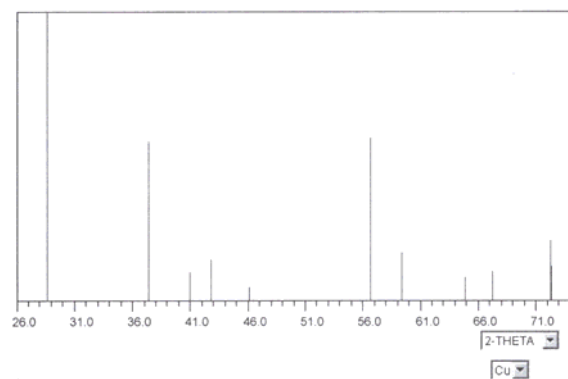
ILMENITE, [1], structure type - ilmenite,  $\text{Fe}(\text{Ti,Mg})\text{O}_3$



Ilmenite

d	I/I°	$\theta$	2 $\theta$
2.728	100	16.4	32.8
2.534	70	17.7	35.4
1.712	52	26.7	53.4

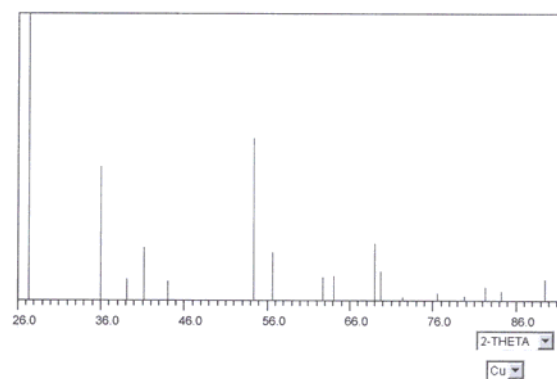
PYROLUSITE, [1], MnO<sub>2</sub>



Pyrolusite

d	I/I°	θ	2θ
3.110	100	14.3	28.6
1.623	56	28.3	56.6
2.405	55	18.7	37.4

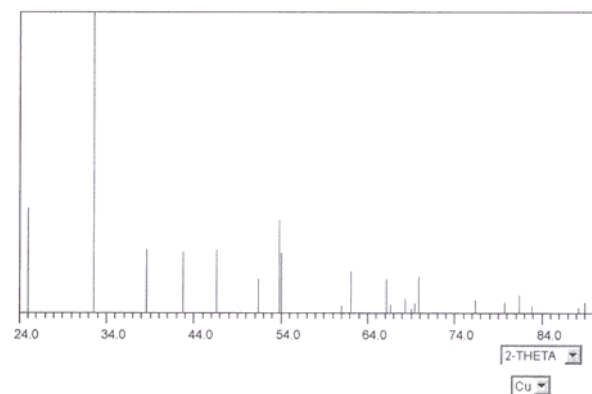
RUTILE, [1], structure type - rutile, at 25°C, TiO<sub>2</sub>



Rutile

d	I/I°	θ	2θ
3.248	100	13.7	27.4
1.687	56	27.2	54.3
2.487	46	18.0	36.1

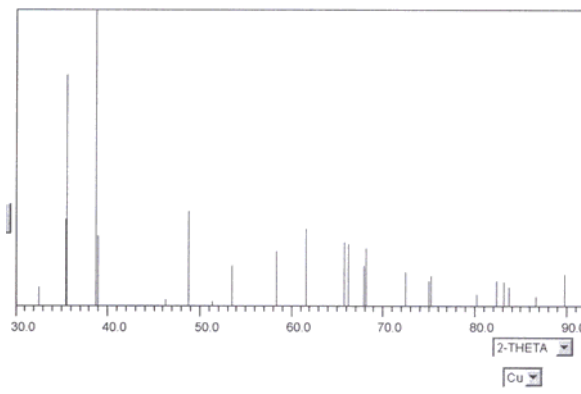
SPHAEROCOBALTITE, [1], CoCO<sub>3</sub>



Sphaerocobaltite

d	I/I°	θ	2θ
2.742	100	16.3	32.6
3.550	34	12.5	25.0
1.702	30	26.9	53.8

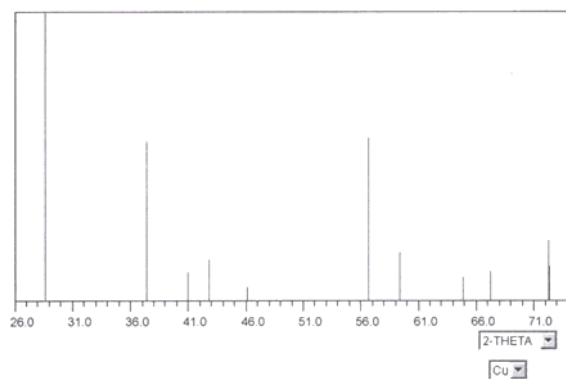
TENORITE, [1], structure type - tenorite, CuO



Tenorite

d	I/I°	θ	2θ
2.322	100	19.4	38.7
2.523	78	17.8	35.6
1.866	31	24.4	48.8

**PYROLUSITE, [1], MnO<sub>2</sub>**

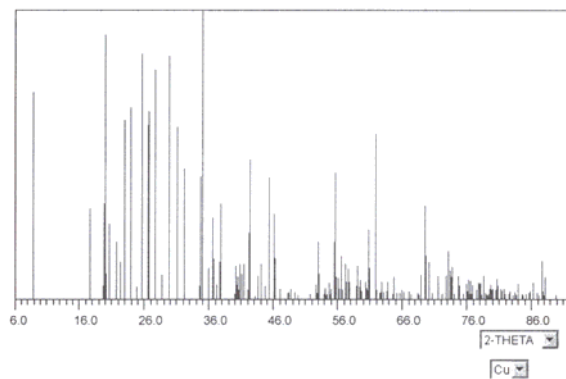


**Zincite**

d	I/I <sup>o</sup>	θ	2θ
2.475	100	18.1	36.2
2.814	55	15.9	31.8
2.602	41	17.3	34.4

**COSMETICS**

**MUSCOVITE, [1], 2M, KAl<sub>2</sub>[Si<sub>3</sub>Al]O<sub>10</sub>(OH)<sub>2</sub>**



Muscovite is used in some cosmetics to provide a pearly-like appearance. Other minerals used in modern cosmetics are rutile and hematite for yellowish and reddish colors respectively. XRD data for these two minerals are found in the preceding section for “Pottery Glazes”.

**Muscovite**

d	I/I <sup>o</sup>	θ	2θ
2.557	100	17.5	35.0
4.448	91	10.0	20.0
3.476	85	12.8	25.6