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DIVISION OF BUILDING RESEARCH

SPECIAL EQUIPMENT FOR MINERAL IDENTIFICATION AND ANALYSIS

by

J. E. Gillott

Report No. 164

of the

Division of Building Research

OTTAWA

November 1959

PREFACE

The need often arises in the work of the Division for the identification of compounds present in soil, bricks, cement and concrete, and plaster, as well as in some of their constituent materials. The provision of the necessary equipment for such analyses was planned as part of the development of the Division. A petrographic microscope was the first to be provided, following recruitment of a member of staff skilled in its use. A beginning was made on the examination of compounds formed by cement-aggregate reactions, but staff changes made it necessary to discontinue this work for a time.

The author, who is specially qualified in the use of petrographic, x-ray, and differential thermal analysis equipment, has recently joined the staff of the Building Materials Section as a Research Officer and has begun a study of the compounds responsible for the abnormal expansion of a particular concrete. The material now reported was prepared in the course of selecting the additional special analysis equipment required by the Division. It forms a useful record and may be of value to others having an interest in such apparatus.

Ottawa
November, 1959

N. B. Hutcheon
Assistant Director

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SPECIAL EQUIPMENT FOR MINERAL IDENTIFICATION AND ANALYSIS

by

J.E. Gillott

SUMMARY

A comparison is made of optical, electron, and x-ray microscopes, and the electron probe x-ray microanalyser is discussed.

A historical introduction to x-ray diffraction is given and the principles underlying the production of x-rays are briefly described. The principal classes of x-ray generator are discussed with particular reference to the micro-focus tube. Methods of recording diffracted x-ray beams by either camera techniques or diffractometry are described, and equipment supplied by the three chief manufacturers is reviewed. There is an account of the applications of x-ray diffraction, with particular reference to the Division of Building Research, and a comparison between diffractometry and film techniques. A layout for the diffraction laboratory and a suggested plan is incorporated.

Thermal methods with particular reference to differential thermal analysis are described.

INTRODUCTION

There are available today many kinds of specialized apparatus for the examination and analysis of material. The optical microscope makes possible visual examination of material under a magnification of 500 times or more. The electron microscope can produce images at magnifications of 1×10^6. The petrographic microscope provides a means of identifying crystalline material through examination of the optical effects produced with polarized light. X-ray diffraction apparatus can greatly extend the range of identification which is possible. Both these techniques have the advantage over conventional chemical analysis in that they identify the compounds present, not merely the anions and cations. Still another method of identification or analysis, differential thermal analysis, makes use of thermal effects as a means of differentiating between compounds.

Some kind of identification or of analysis can best be done by one or another of these methods. In many cases the use of two or more methods provides a more powerful approach, and in some cases may be necessary to provide positive identification. Few laboratories can afford or can justify the use of all of these specialized tools, and it is usually necessary to choose the most appropriate apparatus for the work at hand. The Division of Building Research has had to face such a decision and, in addition, has had to consider making a selection from among the various makes of equipment available. In anticipation of this, it seems desirable to set out, as a first step, a description of the capabilities and limitations of the analysis methods being considered as well as the features of the available equipment. These are now examined and assessed in relation to the anticipated needs. Consideration is also given to the accommodation required for the equipment proposed.

1. MICROSCOPIC EQUIPMENT

The use of a petrographic microscope often makes possible the direct identification of crystalline materials, and mutual relationships between crystals, such as order of crystallization or replacement, may be inferred. Even with an oil immersion objective, however, the resolution limits the useful magnification to about 500 times, although magnifications of 2000 times are often used for convenience in viewing.

The electron microscope has a greater depth of focus than the optical microscope and can resolve details separated by less than 1/10,000 centimetre. A useful magnification of between 1,000,000 and 2,000,000 times is possible. It has been used for the direct observation of dislocations in crystal lattices (31,39) to demonstrate that quartz dust particles are surrounded by an amorphous skin, 10 Å - 50 Å thick (15), and to determine the shapes of small crystals such as the clay minerals. Electrons, however, have only a low penetrating power through solids, and very thin specimens are required for examination. Alternatively, replicas in formvar or collodion, etc., may be employed. As it is necessary for the mean free path of the electron to be longer than the microscope stack, the tube has to be evacuated, and this complicates the examination of hydrated material. The vacuum system commonly needs skilled maintenance.

Research into the design of the x-ray microscope is currently directed towards improving the resolving power, which is not yet equal to that of the electron microscope. However, a high resolution and great focal depth are theoretically possible, and potentially it has advantages in that the specimen does not have to be examined under high vacuum and need not be perfectly dry nor so thin, as x-rays have a greater penetrating power than electrons (12, 40).

Another new analytical tool is the electron probe or x-ray microanalyser. A finely focused electron beam is employed to excite x-ray emission for spectrochemical analysis. Inclusions or crystal zones of the order of 1μ or less (46), may be examined and elements down to atomic number 22, in concentrations of a few tenths per cent, estimated (3).

2. X-RAY EQUIPMENT

X-rays were discovered in 1895 by W. C. Röntgen who was investigating the passage of electricity through a highly evacuated discharge tube. It was realized that x-rays are radiation, electromagnetic in nature, and of much shorter wavelength than visible light. Von Laue suggested that an experimental verification of these ideas would be obtained if x-rays were diffracted on passing through a crystal. Crystals were believed to be composed of an orderly array of atoms, with spacings of the same order as the wavelength of x-radiation. The experiment was performed in 1912 by Friedrich and Knipping. The film, on which the x-rays scattered by the crystal were recorded, showed an orderly arrangement of spots, confirming that diffraction had taken place.

Bragg showed that diffraction occurs only when the following equation is satisfied:

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

where

λ = wavelength
d = lattice spacing
θ = angle of diffraction.

This is the "Bragg Law" that shows, in general, that for a given set of lattice planes, reflection will only take place if there is a variation of either the wavelength of the x-rays (λ) or the inclination of the lattice planes (d). This is the basis of the three principal methods of recording diffraction effects: the powder method; the rotating single crystal method; and the Laue method.

3. PRINCIPLES OF X-RAY PRODUCTION

The production of x-rays is associated with the loss of energy by electrons. Two processes are involved: (1) Loss in energy by collision between cathode-generated high-speed electrons and metal target anode; and (2) Energy losses associated with electronic transitions within the atoms of the target.

(1) This process results in a range of wavelengths. Any particular electron is commonly involved in more than a single collision and this stage-by-stage loss of energy

results in the emission of more than one wavelength. By analogy with ordinary light this is known as white radiation.

(2) The electrons in the target atoms are confined to energy levels which are designated K, L, M, ... denoting the electrons defined by principal quantum number $n = 1, 2, 3, \ldots$. High velocity electrons from the cathode excite the electrons of the target atoms to higher energy levels, and when these fall back to their normal state, x-rays are emitted. If an electron falls from the L to K level the radiation emitted is known as $K\alpha$ and this is of longer wavelength than $K\beta$ radiation associated with the M to K transition. It is impossible to excite the $K\alpha$ wavelength without also exciting $K\beta$. The latter involves a greater energy change and the radiation is of higher frequency and "harder". Emission of this type is known as "characteristic radiation", and the wavelengths are of a definite value depending on the target element.

The characteristic radiation is more intense than the white radiation, which however accounts for a greater proportion of the total energy.

4. GENERATORS

There are two chief classes of x-ray generator:

4.1 Gas Type

In this type, electrons are generated by positive ion bombardment of a light metal such as aluminium. This type of generator is largely of historical interest, although it has certain inherent advantages over the high-vacuum type such as freedom from contamination of the target by tungsten.

4.2 High-vacuum Type

Almost all modern commercial generators are of this type, and electrons are produced thermionically from heated tungsten. A "conventional tube" generates x-ray beams of moderate brilliance, while beams of high brilliance are generated by a "micro-focus tube".

4.2.1 Conventional tube

The manufacturer may incorporate the vacuum as a design feature in some tubes described as "sealed-off" tubes. Alternatively, the tube may be continuously evacuated and described as "demountable".

Both types are manufactured, but the sealed-off tube has become increasingly popular since it has the advantage of ease of maintenance. There is no danger of failure in a vacuum system and no pumping equipment is required. On the other hand, there is a gradual decline in the purity of the radiation obtained since it is impossible to clean the tube, and tungsten evaporated from the filament becomes deposited on the target, giving rise to tungsten L radiation. As it is impossible to change the target, a new tube must be purchased for every radiation required.

4.2.2 Microfocus tube

In general, diffracted x-ray beams are weak and recording times are long. Hence, efforts have been made to increase the intensity or brilliance (quotient of tube power and focal area) of the source.

The main problem is one of cooling the target, which under intense electron bombardment is subject to over-heating, pitting, and corrosion. The problem has been solved in different ways in Russia (Kogan and Pines, see Goldsztaub (17)), France (Goldsztaub (16) and Guinier (20)), and Britain. In Britain, Ehrenberg and Spear (14) achieved a high specific loading (energy per unit area per second) at the focal spot by bringing the electron beam to a small focus to facilitate cooling. They found that if the anode is insulated from the case and held at high positive potential, so that the usual sense of the high tension as between cathode, casing, and anode is reversed, the electromagnetic lens employed by Goldsztaub may be eliminated. This allows a short cathode to target distance, and the influence of stray external fields is reduced.

According to Riley and Stansfield (39), there is an optimum focal width to give high brilliance and high total power, depending on the problem, but a useful general width is given as about 0.1 mm, though a variable focus increases versatility.

As well as providing a more brilliant source, a microfocus allows an improvement in resolution on powder photographs.

By geometrical reasoning it can be shown that at low diffraction angles, line width is directly proportional to the focal width of the x-ray source and the resolution increases with decreasing focal length (37, p.89). If the ratio of camera radius to linear arc breadth is taken as a "figure of merit" defined by P, then the following equations apply:

$$P_A = \frac{E}{m \sin \gamma} \qquad \mu r > 4.0$$

$$P_T = \left\{ 2r \left(\frac{1}{R} + \frac{1}{E} \right) \cos \theta + \frac{m \sin \gamma}{E} \right\}^{-1} \qquad \mu r < 0.25$$

where subscript A refers to an absorbing specimen and subscript T to a transparent specimen

$m \sin \gamma$ = apparent focal length
E = specimen to focus distance
m = focal length
γ = angle at which the focus is viewed
r = sample diameter
R = camera radius
θ = angle of diffraction

The fine focus also increases the peak-to-background ratio as there is less scatter off collimators and slit systems.

The improved resolution is very important in the identification of poorly crystalline materials such as calcium silicate hydrates and some clays (25).

An alternative means of improving resolution by reducing the effective focal area is to employ fine pinholes or slits (collimators), but beam intensity is then reduced in direct proportion (28, p.172).

An apparent reduction of focal width for a relatively smaller loss in intensity is obtained if the target is viewed at a low angle (28, p.168), but there is still an approximate loss of 25 per cent intensity in reducing the viewing angle from 6 to 3 degrees (35).

A fine source of x-rays has other advantages. When a finely focused source of x-rays is used in conjunction with a precision monochromator it is possible to eliminate one component of the $K\alpha_1\alpha_2$ doublet. Their resolution as a doublet in high orders is thus eliminated (6, 37, p.131).

For examining small areas on the surface of a specimen microbeam techniques may be employed utilizing lead-glass capillaries of as little as one-micron diameter. The grain size of fine-grained materials may be determined from spotty ring photographs (37, p.278). To avoid extremely long exposures a fine focus tube of high energy rating is highly desirable (28, p.233).

Diffraction patterns may be obtained from very small amounts of material (12, p.541, para.5), and Banerjee (2) obtained reflections from 6.8 micrograms of gold. He shows that recognizable diffraction effects cannot be obtained from this small quantity of material if a conventional x-ray tube is employed.

When the Debye-Scherrer method is employed an increase of recording speed is possible by reducing camera radius with little loss of resolution. Recording speed is proportional to R^{-3} (37, p.110), the intensity of the diffraction pattern is porportional to R^{-2} (28, p.172) and line breadth to R^{-1}. Thus, by reducing camera radius, a large reduction in exposure time can be obtained for a relatively small increase in line breadth which, with the microfocus tube, is compensated for by the reduction of focal length.

The main disadvantage of the commercially available model is that it is of the demountable type and the vacuum system will involve more maintenance than the sealed-off tube.

5. RECORDING EQUIPMENT

The two principal methods of recording the diffracted x-ray beams are photographic and electronic by means of a diffractometer. The latter produces a "pen recording", graphical in form. Photographic methods were employed first, although an ionization spectrometer was introduced in 1913 by Bragg (4). In the inter-war years photographic techniques were almost universally accepted and it was not until after the Second World War, with improved electronics and the introduction of parafocusing techniques, that interest revived in the alternative method.

5.1 Photographic Recording

No camera described so far gives high quality patterns over the whole range of Bragg angle together with short exposure times, since these results are largely incompatible (28, p.165). Therefore, different cameras are used for different applications. These cameras employ the Debye-Scherrer technique, focusing techniques, glancing angle and flat layer techniques and back-reflection techniques. There are also special cameras for single crystal work.

5.1.1 Debye-Scherrer cameras

This type of camera is most generally useful and is most commonly employed.

If θ is the angle between a reflecting plane and the direct beam, then the diffracted beam makes an angle of 2θ with the direct beam. In the case of a crystalline powder a particular set of planes may be assumed to occupy all orientations in space, and the diffracted beams lie on cones of semi-angle 2θ about the main beam. In the Debye-Scherrer arrangement a crystalline powder specimen is surrounded concentrically by a film-strip on which is recorded the equatorial section of the cones of diffracted x-rays corresponding to different lattice spacings. Commercial cameras are designed to give a reasonable compromise between intensity of diffraction and resolution over a wide angular range (28).

The Debye-Scherrer method has the advantages of simplicity and the recording of all reflections on one film at the same time. When it is required to record reflections with either high θ values, to measure cell parameters accurately, or low θ values, as in the case of clay minerals, some hydrated calcium silicates, and aromatic hydro-carbons, a modification of the technique becomes necessary.

5.1.2 Focusing techniques

Much of the recorded background is due to diffraction of white radiation which may be almost wholly eliminated by the use of a crystal monochromator. In addition, harmonics of wavelengths $\lambda/2$ (λ = wavelength), which otherwise still occur, can be greatly reduced by keeping the value of μt small for the specimen (18) (μ = linear absorption coefficient, t = specimen thickness).

According to Brindley (37, p.122), "for the elucidation of the finer points of x-ray diffraction diagrams, crystal reflected radiation is practically essential". In the Guinier camera the x-rays are both monochromatized and focused. The sharp focusing of the diffracted beams, together with the effective doubling of the camera radius, gives increased resolution. In this type of camera a large surface area of the powder specimen is irradiated and this tends to shorten exposure times and compensates for the reduced intensity of the crystal monochromatized incident beam. Line broadening due to specimen size is also largely eliminated (47, p.411).

The main disadvantage of cameras of this type is that only a limited angular range of reflections may be recorded with any one camera.

5.1.3 Glancing angle and flat layer techniques

Powder samples tangential to the focusing circle give a beam focused over a restricted angular range which may be varied by changing the angle between incident beam and powder sample. This principle is utilized in cameras of the Brindley type and in the diffractometer. In work on clay minerals, for example, the low-angle region of reflection is particularly important, and the gain in resolution due to focusing outweighs the loss of the high-angle reflections which are sacrificed in Brindley cameras. This camera is simpler and probably easier to use than a Guinier-type camera.

5.2 The Diffractometer

The same focusing principle is employed as in the Brindley-type camera, but focusing is maintained throughout the entire angular range by rotating the detector about the sample with twice its angular velocity. Thus, throughout the entire angular range the sample surface remains tangential to the focusing circle, which decreases in radius as the detector scans towards higher angles.

A Geiger-Müller counter, proportional counter, or a scintillation counter may be used to detect the diffracted x-ray beams. Each of these has advantages, depending on the application (36), but until recently the Geiger counter has been most commonly employed.

5.2.1 The Geiger-Müller counter

In essence this consists of an anode wire maintained at a potential of the order of 1000 to 1500 volts from the coaxial cathode. The tube assembly is filled with a gas, such as argon or krypton, which has a high specific ionization and high absorption for x-rays. The arrival of x-rays ionizes the gas, and secondary processes due to the high potential lead to discharge along the whole length of the anode wire (9, 13). In the absence of quenching continuous discharge would result. The positive ions produced in the ionization process move more slowly than the electrons, and a measureable time, the "recovery time", must elapse between the recording of an initial pulse and a later pulse to allow for this migration of positive ions. At high counting rates, pulses arriving during the "dead-time" will not be recorded, leading to a non-linear response by the Geiger counter. For accurate work at high counting rates these losses must be allowed for, and according to Arndt (37, p.196) this is most readily achieved if the Geiger counter is quenched by means of an external multivibrator-type circuit of known dead-time characteristics.

The Geiger counter shows no relationship between pulse amplitude and x-ray energy, although there is a rough wavelength selectivity of response since window transmission falls at longer wavelengths and gas absorption is less efficient at shorter wavelengths.

5.2.2 The proportional counter

This differs from the Geiger counter in that it operates at a lower potential between anode and cathode. It has the effect of limiting the discharge to the region of the plane normal to the cathode wire at which the initial ionization took place. Hence, there is a proportionality between initial ionization and total discharge current. This eliminates the problem of the determination of "dead-time", and by utilizing an electronic pulse-height analyser it is possible to improve the peak-to-background ratio. By the correct choice and setting of detector-discriminator combination a large measure of monochromatization may be achieved. According to Parrish and Kohler (36), however, there are certain special cases in which it is still preferable to employ a crystal monochromator, but for most applications it is unnecessary if electronic discrimination is available.

5.2.3 The scintillation counter

This detector has a higher quantum counting efficiency (the percentage of incident monochromatic x-ray quanta which produce detectable electrical impulses) (36) than the other two, and with pulse-height discrimination it rates as the best detector for Mo-, Cu-, and Co- radiations (36). If pulse-height discrimination is not available, however, it gives high backgrounds. On the other hand, the proportional counter has a higher energy resolution which is an advantage when discrimination against wavelengths near those being recorded is desired (36).

6. MANUFACTURERS

There are three main suppliers of x-ray equipment: North American Philips Co., General Electric Corporation and Hilger and Watts. Philips and General Electric are American Manufacturers and Hilger and Watts manufacture in England.

6.1 Generators

Philips and G.E. both produce x-ray generators with sealed-off tubes of conventional type. The only microfocus unit on the market is produced by Hilger and Watts.

6.2 Recording Equipment

6.2.1 Cameras

Excellent Debye-Scherrer cameras are produced by the three major manufacturers and also by other firms such as Unicam, Cambridge, England.

Focusing principles are embodied in the Guinier camera produced by Nonius-Hilger-Enraf, Delft, Holland, in which four specimens may be simultaneously examined, their diffraction patterns being recorded on one film. This is particularly convenient for comparison purposes. This camera covers an angular range of 0 to 45 degrees Bragg.

A Brindley camera specially designed for use with the microfocus unit is manufactured by Hilger and Watts.

A fine camera for recording high-angle reflections is produced by the Picker X-ray Corporation (28, p.217).

The General Electric Corporation produces a monochromatic pinhole camera which records the complete diffraction circles at low angles. This is useful for the examination of halos produced by amorphous and vitreous materials.

6.2.2 Diffractometers

Each of three major manufacturers of x-ray equipment produces a diffractometer, together with the electronics required for recording. Each has certain points in its favour.

The North American Philips diffractometer is mounted so that the detector scans in a vertical plane. In most texts this plane is referred to as the "horizontal plane" and diagrams must be rotated mentally through 90 degrees. The arrangement is less readily adapted to high or low temperature studies than are horizontally mounted units (see, however, Refs. 8 and 10). The direct beam is not monitored. The three types of detectors are supplied together with the electronics required for pulse-height discrimination, however, and in this respect this equipment is probably the most advanced.

The General Electric Co. supplies a large diameter diffractometer mounted in the horizontal plane. It is of massive construction and should be readily adaptable to high or low temperature work. A proportional counter is available with a reverter. A scintillation counter is not produced; the direct beam is not monitored; and scanning speed is less conveniently changed.

Messrs. Hilger and Watts produce a diffractometer mounted in the horizontal plane, which is of smaller dimensions than the one produced by the General Electric Co. Scintillation counters are available and there is provision for pulse-height discrimination. The direct beam is continuously monitored by a second detector, and fluctuations in output from the x-ray tube are automatically corrected for on the chart graph by the ratio recorder.

For quantitative work the Hilger arrangement of monitoring the incident beam is, in the writer's opinion, superior to arrangements which depend on a stabilized x-ray generator.

7. APPLICATIONS OF X-RAY DIFFRACTION

Oriented single crystals, crystalline powders, and polycrystalline materials give the most easily decipherable x-ray diffraction patterns, but radial distribution analysis also enables gases, liquids, and amorphous solids to be investigated (24). Amorphous materials such as iron oxide gels, which undergo a thermal reaction, are however, more readily investigated by differential thermal analysis (30).

7.1 Identification of Minerals

The standard preliminary to the x-ray analysis of crystalline materials is observation under the petrographic microscope, which is important for two reasons: that minerals may be directly identified if of sufficiently large grain size; that by hand picking it is often possible to concentrate an unknown phase, thus greatly facilitating interpretation of the x-ray diffraction pattern. When the grain size is less than about 10^{-3}mm, however, little can be expected from optical examination.

Identification by x-ray diffraction differs from chemical analysis in that phases, not elements or radicals, are described. Thus the three minerals, rutile, anatase, and brookite, differ crystallographically and in their properties, but all have the same chemical composition, TiO_2. Calcite and aragonite, both of chemical composition $CaCO_3$, are other common examples, as is iron rust, composed of géothite and lepidocrocite, chemical formula FeO(OH). This compound forms a third polymorph, apparently stable only in the presence of Cl negative ions (37, p.500). On the other hand, materials that differ chemically may give similar diffraction patterns if the internal atomic arrangement is similar. The spinels fall into this category.

Crystalline materials are characterized by their lattice spacings (d - values), and these have been determined for a large number of substances. This knowledge is the basis for identification by x-ray methods. There are various systems, but the one most commonly employed is the ASTM card index. This is a joint undertaking by the American Society for Testing Materials, The American Society for X-ray and Electron Diffraction, and the British Institute of Physics. In this index every pattern is represented by three cards corresponding to the three strongest lines in the diffraction pattern.

The ASTM system has certain limitations. Solid solutions have variable lattice parameters depending on substitutions in the cell. Hence, many extra cards would be required to ensure that intermediate members of a solid solution series, whose d-values differ considerably from those of the end members, are not missed. The ASTM system is also based on the "strength" or intensity of the lines; this may vary because of factors such as internal lattice strains, small crystallite size, and substitutions in the lattice.

7.1.1 Clays

According to Grim (19), the upper-size limit of the clay-grade in sediments is about 2 microns. Thus, the optical microscope has limited applicability and x-ray investigations are almost limited to the powder method. The most complete data are contained in "X-ray Identification and Crystal Structures of the Clay Minerals" edited by G.W. Brindley (7).

Many of the clay-minerals are built up of sheets of atoms linked by relatively strong bonds within the sheets but bound only by weak forces to neighbouring sheets. This produces imperfections which may take the form of displacements in two directions parallel to the sheets or interstratification of layers of different kinds. The interstratification in these mixed-layer structures may be either regular or irregular (19, p.86). Regular interstratification results in an apparently larger unit cell, as in the chlorites. Irregular mixed-layer structures result in a non-integral series of basal reflections, the positions and intensities of which vary, depending on the proportions of the constituents. This variation is not necessarily linear (19, p.104).

For identification of clay minerals the basal series of reflections is the most important, and the Debye-Scherrer powder technique is frequently inadequate owing to the long spacings which have to be recorded. Techniques which give a high peak-to-background ratio are essential for best results.

Auxiliary techniques such as heat treatment, or treatment with acid or organic liquids, are often necessary for identification. Additional information may be obtained from differential thermal analysis (30, 42) and electron microscopy.

In the Division of Building Research, clay minerals are likely to be of interest to workers in the Materials Section and in the Soil Mechanics Section. The clay minerals form varying proportions of sedimentary rocks, used as aggregate in concrete, and are the raw materials for the brick industry. They have an important influence on the mechanical and engineering properties of soils. In Canada, however, rock flour of clay-size grade composed of non-clay minerals frequently contributes significantly to the mineralogical composition of soils (38).

7.1.2 Cement minerals

Minerals present in cement clinker are generally identified by a combination of optical and x-ray methods. Etch reactions and reflected-light techniques are used in conjunction with transmitted light and x-ray diffraction (33).

Calcium silicate hydrates are similar to clay minerals in that long spacings sometimes have to be recorded. They also may give weak diffraction patterns and, if present in conjunction with well crystallized phases, are likely to be missed. Tobermorite, for example, was not identified as a product of set cement until it was concentrated by centrifuging and the light fraction was examined with the microfocus x-ray tube and focusing cameras (25). According to Kalousek and Prebus (26) there are three very similar calcium silicate hydrates that serve as binders in concrete; to distinguish among them satisfactorily it is necessary to employ differential thermal analysis, electron microscopy, infra-red absorption, the stability to aceto-acetic ester and the mineral's oxide composition, in addition to x-ray diffraction.

7.1.3 Paint manufacture

The determination of polymorphous forms of pigments of the same chemical composition is important. In many cases it determines: differences in opacifying power; differences in photochemical reactivity with the organic binder, leading to differences in the durability of paint; differences in the colour stability of the pigment, leading to fading, darkening, or other colour changes of paint.

The determination of phases present in pigment mixtures is also desirable, as is the elucidation of the physical structure of resins, oils, and paint films (21). The strongest line of fatty acids, greases, and soaps frequently has a long spacing which will be missed unless special techniques are employed.

7.1.4 Plaster of paris

Plaster samples may be examined to determine the presence of hydrates of gypsum, calcium carbonate, and other minerals. The rate and extent of hydration may be investigated and attempts made to determine quantitatively the proportions of the various hydrates in, for example, hardened wall plaster (34).

7.2 Accurate Determination of Intensity of Reflection

The intensities of the individual reflections may be estimated by eye, or more accurately by a micro-densitometer, if film techniques are employed, or recorded directly on the diffracted beams with counters.

7.2.1 Quantitative estimation of mineral phases

An estimation of the percentage of a mineral species in a mixture may be made under favourable circumstances. It depends upon the fact that the intensities of the powder patterns are proportional to the quantities of the phases present.

Two methods are available:

A series of standard mixtures may be prepared and a correlation made between the intensities of reflections and quantities of materials (28, p.410-39).

The reflected intensities may be calculated from the structure factors (37, p.338), if the crystal structures of the components of the mixture are known.

The reproduceability of results of these techniques is not high (about 2 per cent at best) and with clay minerals the method is particularly difficult because of structural imperfections in the minerals (6); other techniques, such as determination of potassium content, total surface area, or exchange capacity (5) are often easier.

On the other hand Goldschmidt and Richardson (37, p.559) report that the method has been successfully employed in checking correct firing history and composition of raw materials in the production of fire bricks and silica or basic refractories; and Copeland (11) claims that quantitative analysis of portland cement by x-ray diffraction techniques is superior to microscopic methods.

7.2.2 Line profiles

The form of the individual reflections is influenced by the geometry and instrumentation of the experimental arrangement and by the nature of the scattering material. Estimates may be made of the sizes of the crystallites and information may be obtained on distortions and defects within the lattice. For example, random-layer structures resulting from displacements between the layers lead to characteristic line profiles (46). The intensity distribution may be determined either by micro-densitometry using film techniques, or more directly, by a suitably designed diffractometer (22) and information obtained on the lattice imperfections.

7.2.3 Structure determination

The whole subject of the determination of atomic positions within the space lattice rests largely upon the estimation of the intensities of the scattered x-ray beams.

7.3 High Temperature Transformations

X-ray crystallography has two main applications at high temperatures - to follow phase changes and to measure thermal expansion. It has an advantage over other methods in that the behaviour of individual phases may be followed.

Studies on brick manufacture and cement clinker at a specific temperature or at steadily rising temperatures may be undertaken. Taylor reports work on the dehydration of tobermorite and its conversion into xonotlite (44).

7.4 Low Temperature Investigations

Equipment may be adapted to diffraction experiments at low temperature, and changes in the properties of ice crystals have been investigated by this technique.

7.5 High Pressures

By encasing materials in a pressure bomb constructed of beryllium, Lawson and Riley (29) report that phase changes at high pressures (15,000 atmospheres) may be investigated. The beryllium is relatively transparent to x-rays.

7.6 Stress Measurements

This technique has been employed mainly in investigations on metals. It depends upon the measurement of lattice strains and their interpretation in terms of stresses. Cullity (13) states that shear stresses cannot be estimated and that only normal stresses are measurable. Klug and Alexander (28, p.540) point out that diffraction procedures determine only elastic stresses; and G.B. Greenough (37, p.609) remarks that since a lattice strain persists after plastic extension then these parts must be stressed, because this is the only way in which atoms can be held out of their equilibrium positions. He suggests that this may indicate different yield stresses in different parts of the specimen. The implication that micro-stress systems exist is apparently under active discussion, and it is likely to be important for a clearer understanding of fatigue and corrosion, particularly along grain boundaries.

7.7 Single Crystal Work

More crystallographic information can be obtained by the study of single crystals than of powders, especially in the lower systems of symmetry.

7.8 Preferred Orientation Studies

When mineral aggregates recrystallize under directional stress they frequently show preferred crystallographic orientation. This may be determined.

8. COMPARISON OF THE DIFFRACTOMETER WITH FILM TECHNIQUES

Both film techniques and diffractometer recording have advantages, depending on the application.

8.1 Identification

In many ways a camera technique is preferable to the use of a diffractometer. Films are of convenient size for visual comparison with standard patterns, a particularly conclusive way of confirming an identification and one which may be carried out by relatively untrained personnel. A diffractometer recording giving the same degree of detail is of unwieldy length, and there are more variables which affect the sensitivity.

Preferred orientation in the sample is utilized as an aid to identification in the case of platy minerals such as the clays. In other groups , however, it is necessary to avoid preferred orientation in the minerals composing the sample, since this affects line intensities on which relies the identification system based on the ASTM index. It is more difficult to avoid preferred orientation in sample preparation for diffractometry than for a Debye-Scherrer camera. Preferred orientation is more readily detected on film than on a diffractometer recording.

When more than one phase is present in a sample, differences in hardness between the constituents may lead to the harder phase, which is more resistant to crushing, exhibiting "spotty" diffraction lines. The lines then characterize the harder phase. There is no similar result on a diffractometer recording.

On the other hand, the diffractometer recording is quicker, especially in an investigation of only a limited angular range, as when a sample is subjected to auxiliary techniques which are known to affect only certain lines in the diffraction pattern. This application mainly concerns the clay minerals.

8.2 Accurate Determination of Intensity of Reflection

The diffractometer is probably superior to film techniques since relative intensities are directly recorded in only one process. A few lines may be selected and scanned point-by-point, the counts having been predetermined to give a desired statistical accuracy.

8.3 High Temperature Transformations

The diffractometer, if of appropriate design, may be readily adapted to this work. A special high temperature camera is required for film techniques and there is a danger of film shrinkage or expansion. Also, rapid phase changes may be followed by the diffractometer by recording intensity changes or changes in position of a given line. Quenching is thus avoided.

8.4 Stress Measurement

This involves the accurate measurement of small changes in lattice parameter. Reflections at high angles are most sensitive to such changes, and at present a "back reflection camera" is likely to give better results than a diffractometer.

8.5 Preferred Orientation Studies

The diffractometer technique is superior to the use of film since pole figure charts are eliminated and the process is faster.

9. CONCLUSIONS ON EQUIPMENT

It is suggested that a Hilger and Watts microfocus x-ray set should be selected, together with a diffractometer and a Nonius Guinier camera, a Brindley camera, and a general purpose camera.

The diffractometer electronics are frequently modified to incorporate a triple-gate ratio recorder. This automatically records either the time for a selected number of counts or stops the count after a predetermined time. It would also be desirable to incorporate the necessary modifications in the electronics for the use of scintillation counters with pulse-height discrimination.

10. THE DIFFRACTION LABORATORY

Soft x-rays such as those employed in x-ray diffraction are heavily absorbed by tissues (23), and exposure to the direct beam of an x-ray set will cause severe burns. The scattering of the direct beam by walls, etc., and air in the laboratory leads to an increase in background which also produces a cumulatively harmful effect. Handbooks laying down acceptable standards of safety have been issued in Britain and the U.S.A. The permissible daily dose of x-radiation is given as 0.05 roentgen. (The roentgen is that quantity of radiation which will produce 2.1×10^9 ion pairs in a cubic centimetre of air (1)). Most modern x-ray sets are constructed to keep scattered radiation to a minimum and most cameras are very well designed in this respect. By its nature, shielding is less easy with the diffractometer, but a simple arrangement of hinged lead sheets can be contrived which is relatively efficient. Regular monitoring of the laboratory should be a routine procedure.

In the layout of a diffraction laboratory it is advisable to segregate the x-ray generator from the office space, if possible, to reduce chance exposure to radiation. Klug and Alexander (28) give a suggested layout for a diffraction laboratory (Fig. 1), the minimum space requirements for one man being 300 square feet.

Figure 2 shows a suggested arrangement of equipment likely to be required in mineralogical investigations.

11. THERMAL EQUIPMENT

The most commonly employed thermal methods of analysis are based on measurement, separately or in combination, of weight changes, dimensional changes, or energy changes. Thermo-balance curves, dilatometry, and differential thermal analysis are the most common methods of recording changes in these fundamental properties. Differential thermal analysis differs from thermogravimetry in that it can detect changes such as crystal inversions and recrystallization in addition to reactions leading to weight changes, though a simultaneous recording of both on the same scale gives more information than either independently. Dilatometry has not been extensively used for identification.

In general, material is powdered for differential thermal analysis and the effect of a constant heating rate on the unknown is compared with a similarly placed, powdered, inert standard. The temperature difference between the two is measured by thermocouples, and a reaction or transition in the sample is recorded as a peak on the graph of temperature difference against time or temperature difference against temperature.

The identification of materials by the differential thermal technique depends upon the near constancy of the peak temperature at which a reaction commonly takes place, and as the peak area is proportional to the amount of reacting substance, quantitative analysis may be possible.

To be detected a component must normally be present in a concentration of 1 to 2 per cent (41, p.41), but for certain minerals such as the carbonates the sensitivity is higher and this usefully supplements x-ray analysis which may fail to detect as much as 5 per cent $CaCO_3$ (30, p.329). Amorphous materials which undergo a thermal reaction are more readily detected than by x-ray diffraction. Additional information is provided in clay mineralogy (30, p.19, 261, 271; 41, p.70, 145), in chemical kinetics (27; 30, p.82, 395; 41, p.131, 135), the reactivity of solids (41, p.126), and in geological thermometry (41, p.125).

The main limitations of differential thermal analysis arise from difficulties in interpretation of curves. For example, a peak temperature may vary because of differences in heating rate, packing of specimen, differences in type of specimen holders, and amount of reactive material. Differences in composition or structure between different specimens of a mineral and small amounts of admixture (41, p.67) may have large effects on the form of the heating curve. In mixtures, overlapping peaks may be difficult to resolve.

Equipment comprises sample holder and block, thermocouple, furnace, heating rate controller, and recorder. It is often constructed in individual laboratories and there is considerable variation in the component details. This leads to difficulty in comparing curves recorded on different instruments, though the specimen holder and block and temperature regulating system probably have the greatest effect (30, p.23).

The sample holder and block may be of either metallic or ceramic construction. Ceramic holders give larger peaks and better reproduceability up to about 650°C, but above about 750°C reproduceability is better with metallic holders (32, 30).

The thermocouples may be of base metal or noble metal construction. Base metals give a higher sensitivity and are cheaper. Noble metal thermocouples may be used for higher temperatures and are less likely to react with the sample.

The furnace should provide for adequate heating, low thermal gradients, and rapid heat transfer. Symmetrically located, electrically balanced coils designed to reduce induced electromotive force in the thermocouple circuits may be an advantage (42). There should be some system for accurate positioning of the sample holder and block.

The program controller is probably the most important component of the apparatus, as it must ensure a reproduceable temperature rise. It is desirable that the heating rate should be variable, but the controller should accurately follow a predetermined cycle. Devices which vary the current or voltage supplied to the furnace have been employed, but a variable energy input proportional to the amount of overheating or underheating is considered most satisfactory (30, 44).

Both photographic and automatic chart recorders are employed. The photographic recorder may have a very high sensitivity, but as the progress of the analysis cannot be directly followed, it is not possible to make adjustments during the analysis. According to Mackenzie (30, p.38), it is best to record temperature difference against temperature of sample rather than against time; this may be accomplished by use of an X-Y recorder.

Atmospheric control increases versatility and facilitates interpretation of curves. Most commercial equipment has provision for flooding the sample holder with inert gases, but the dynamic atmosphere system described by Stone (43) is probably the most advanced. In reactions from which a gas is evolved it is possible, under favourable circumstances, to determine the heat of reaction, and this may be useful for mineral identification as more data are accumulated.

There are now several models available commercially, including the "Deltatherm" produced by Technical Equipment Corporation, U.S.A., the controlled dynamic atmosphere equipment of R. L. Stone Co., Texas, U.S.A., the Linseis Differential Thermoanalyzer manufactured in Germany, and the Philips model manufactured in Holland. In addition, Leeds and Northrup produce a temperature controller and recorder but not a furnace or specimen block.

The Philips model is the simplest and cheapest. However, the program controller is not considered capable of giving a reproduceable temperature rise and there is little to recommend it.

The "Deltatherm" is restricted to a maximum temperature of 1100°C and there is no continuous recording of temperature. This is indicated by blips at 100°C intervals on the differential chart. The atmosphere in the furnace may be varied dynamically. The cost price is about the middle of the range, but the newest electronic feedback controller is likely to be more expensive.

Leeds and Northrup manufacture equipment which can be employed for the controller and recorder of a differential thermal analysis set-up. The furnace, sample holder, and thermocouples would have to be obtained elsewhere.

The Linseis apparatus records both temperature difference and temperature on the same chart and may be operated up to a temperature of 1550°C. The equipment has provision for atmosphere control and may be adapted for simultaneous recording of both differential thermal and weight loss curves. The sensitivity may be varied from 1/1 to 1/20. The temperature controller operates as a resetting regulator. The cost price is about the middle of the range of the instruments available.

The equipment of R. L. Stone is supplied with a powerful amplifier which enables weak reactions to be investigated, the limits of adjustment being about 1000:1. Stone finds, however, that this high amplification leads to spurious effects on the chart with any of the conventional controllers, and the temperature rise is achieved by means of a saturable core transformer, although reproduceability is not high. Temperature is recorded by marks at 100°C intervals on the chart of differential temperature, and is also recorded continuously on a separate chart. The most attractive feature of the equipment is its great versatility with respect to pressure (1.0 mm Hg to 100 psi (85 psi gauge)) and atmosphere control. The gases are passed through the sample so that the atmosphere in contact with the particles of powder is known.

Either constant pressure or temperature may be employed and the other variables abruptly changed. The maximum temperature attainable is 1400°C. This is the most costly of the instruments described.

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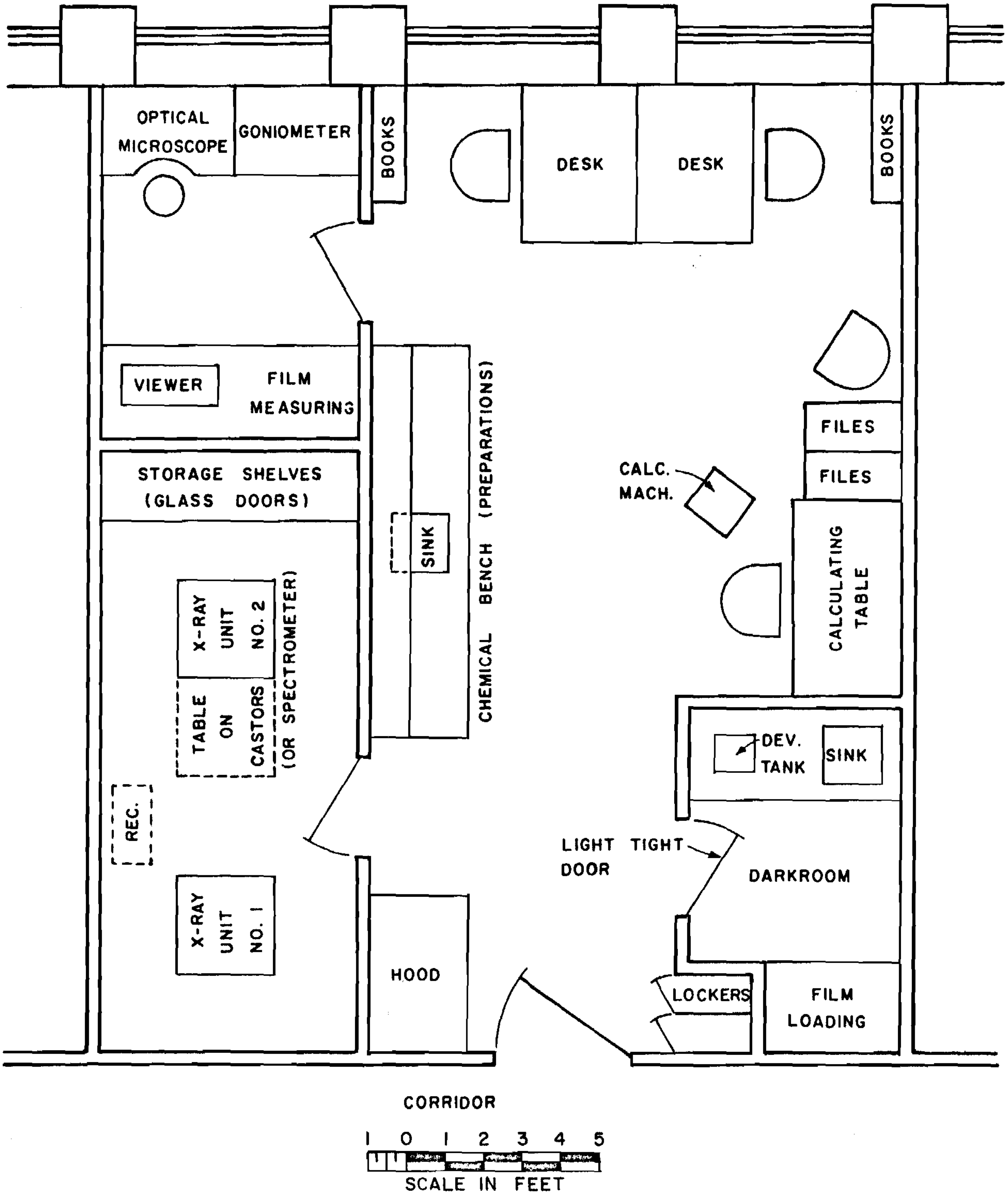

FIGURE I

PLAN OF AN X-RAY DIFFRACTION LABORATORY FOR TWO WORKERS

(FROM KLUG, H.P., AND L.E. ALEXANDER. X-RAY DIFFRACTION PROCEDURES FOR POLYCRYSTALLINE AND AMORPHOUS MATERIALS.)

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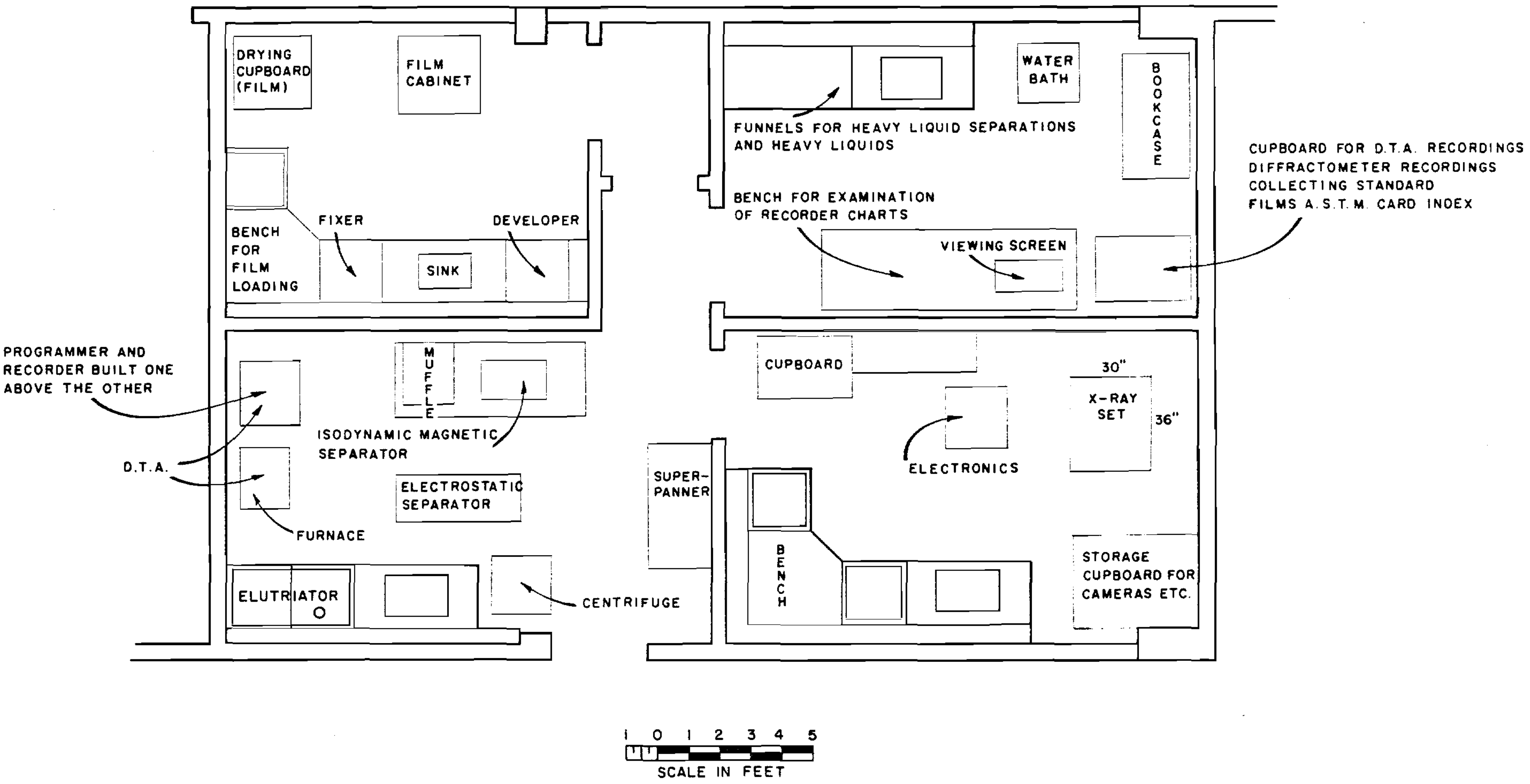

FIGURE 2

LAYOUT OF DARKROOM AND LABS