MINERAL SEPARATION TECHNIQUES

(DAMM, V 1.0; 09-87)

The sole emphasis of this pamphlet, which is based mainly on the experience of the author and is everything but complete, is to give you an idea what might be done by now and in which way in our new mineral separation lab. Since it is also directed to the very "beginner" you might find some explanations or advices redundant. The author in any case would deeply appreciate any comments or suggestions concerning the methods described and asks the reader to close his eyes on the all too obvious language mistakes.

I. PREPARATION OF SAMPLES

Techniques used for mineral separation depend upon the purpose of analysis and whether or not the sample is unconsolidated, poorly or fairly consolidated, or, is a well lithified sedimentary rock or a crystalline rock. Some projects require determining weight percentages of various minerals in a sample, and also an examination of the shapes and surface textures of minerals. Other projects require the separation of clean, virtually pure concentrates of individual minerals for chemical analysis without regard for mineral morphology. The below briefly described operations are applicable to sediments as well as hard rocks, even so initial handling procedures may differ.

a. UNCONSOLIDATED or WEAKLY CONSOLIDATED ROCKS:

First grains must be cleaned of adhering fine-grained particles, such as clay coatings on feldspars. Beach and river sand grains are usually fairly clean. After sieving, put the sample in a beaker of destilled water and place it in a sonic vibrator. The sonic vibrator scrubs individual particles, cleaning them of

adhering finer-grained material. If adhering material is an oxide or carbonate, chemical treatment is necessary. Fe-oxide coatings may be removed by dilute HCl (1:5 H_2O), but avoid prolonged treatment, especially if metasilicates are present. Dilute acetic acid (1:1 H_2O) will generally dissolve carbonates. If the purpose is to examine the morphology and surface markings on grains, do not leave them in a sonic vibrator more than $1^1/_2$h to 2h or in acids too long!

Partially consolidated rocks require additional operations before scrubbing in a sonic vibrator or acid treatments:

- Break them by gentle crushing (not grinding!) in a clean mortar and pestle, especially if shapes and surface textures are to be studied;
- screen the broken rock through a 2mm sieve to eliminate small particles that are broken by crushing;
- place the pea- and walnut-sized fragments in a jar containing a steel roller and about a teaspoon of dispersing agent (e.g.: sodium hexametaphosphate), fill the jar with water and roll the jar for 1h to 2h on a jar mill;
- wash the sediment through a 60µm (250mesh)-screen (save the finer-grained material for possible pipette analysis);
- scrub the sand in a sonic vibrator for further cleaning;
- the sample is now ready for sizing by sieving and further operations.

b. HARD ROCKS (SEDIMENTARY or CRYSTALLINE):

Any separation of minerals from hard rocks requires **initial crushing**, **sieving** and **cleaning**. The size (or weight) of rock needed for getting mineral separates varies according to rock type and the purpose of analysis. Generally 500g will be enough for fine- to medium-grained silicate rocks. However, special operations like separation of zircon populations for U/Pb age determination might require sample sizes in excess of 500kg.

Preliminary thin section examination is highly advisable to determine the approximate percentage and grain size of minerals, in the rock samples. This will help to establish what mesh size(s) the sample is to be ground. The mesh-size needed for mineral separation depends on the grain size, inclusions, zoning and intergrowths. The sample should be ground fine enough to release the particular mineral from its inclusions or intergrowths. If particular zones are to be separated in zoned minerals, the material should be as fine as the zone widths.

If minerals are different in hardness or size in the same specimen, a preliminary concentration can be done during grinding. In a garnet-chlorite schist, for example, the garnet will be concentrated in the coarse fraction and the chlorite in the fine. In granitic rocks, the accessories often occur in the <180µm (<80mesh)-fraction.
It is furthermore important to work with a uniform-sized sample in mineral separations because the techniques described below depend on physical properties for separation. These properties or forces do not react uniformly with material of unequal size, particularly magnetic separations where the same mineral of different size may be preferentially separated by magnetic attraction.

Crushed material is best sized by sieving, but guard against contamination, particularly with brass sieves which may introduce solder and metal fragments. Sieves should be washed with destilled water after each operation to remove adhering fragments in the mesh. Disposable PTFE sieve nets held in cut PP bottles (or wharever acetone-resistant is at hand!) is a more satisfactory method of sieving because little or no contamination is introduced. Remove all the fine particles once the required mesh-size is attained. This may be done by elutriating the mineral grains in aqua dest./ethanol/methanol or acetone or scrubbing them for 1h to 2h in a sonic vibrator.

Many rocks contain alteration products which interfere with the mineral separations. Iron oxide and carbonates may impregnate or

surround the mineral grains. Gentle acid treatment will remove this undesirable material (see earlier discussion!). The so prepared samples are ready for further operations.

II. MAGNETIC SEPARATION (FRANTZ ISODYNAMIC SEPARATOR)

1. INTRODUCTION:

The Frantz separator is extremely versatile and can produce excellent concentrates of many minerals. However, some caution should be taken in its use and in most cases, it is advisable to centrifuge separates from the Frantz before they are used for analytical work.

It may be furthermore suggested to the user, to take the time and read this pamphlet carefully, as it will save him delay and frustration.

2. FUNDAMENTALS:

Magnetic susceptibility is an important property of minerals. Minerals are **paramagnetic** when magnetic force lines pass through them more easily than through air, and are **diamagnetic** when they pass readily. Besides this general description, there are six different types of magnetic materials (feel free to skip this over!):

DIAMAGNETIC: THOSE WITHIN WHICH THE MAGNETIC INDUCTION IS SLIGHTLY LESS THAN THE APPLIED MAGNETIC FIELD; DIAMAGNETISM IS AN ATOMIC SCALE CONSEQUENCE OF THE LENZ-LAW OF INDUCTION; FOR DIAMAGNETIC MATERIALS, THE PERMEABILITY IS SLIGHTLY LESS THAN THAT OF EMPTY SPACE, AND THE MAGNETIC SUSCEPTIBILITY IS NEGATIVE AND SMALL.

PARAMAGNETIC: THOSE WITHIN WHICH THE MAGNETIC INDUCTION IS SLIGHTLY GREATER THAN THE APPLIED MAGNETIC FIELD; PARAMAGNETISM ARISES FROM THE PARTIAL ALIGNMENT OF THE PERMANENT MAGNETIC DIPOLE MOMENTS OF ATOMS OT IONS; THE PERMEABILITY IS SLIGHTLY GREATER THAN THAT OF EMPTY SPACE, AND THE MAGNETIC SUSCEPTIBILITY IS POSITIVE AND SMALL.

FERROMAGNETIC: THOSE IN WHICH THE MAGNETIC MOMENTS OF ATOMS OR IONS IN A MAGNETIC DOMAIN TEND TO BE ALIGNED PARALLEL TO ONE ANOTHER IN ZERO APPLIED FIELD, BELOW A CHARACTERISTIC TEMPERATURE, CALLED THE CURIE POINT; COMPLETE ORDERING IS ACHIEVED ONLY AT THE ABSOLUTE ZERO OF TEMPERATURE; WITHIN A MAGNETIC DOMAIN, AT ABSOLUTE ZERO, THE MAGNETIZATION IS EQUAL TO THE SUM OF THE MAGNETIC MOMENTS OF THE ATOMS OR IONS PER UNIT VOLUME; BULK MATTER, CONSISTING OF MANY SMALL MAGNETIC DOMAINS, HAS A NET MAGNETIZATION WHICH DEPENDS UPON THE MAGNETIC HISTORY OF THE SPECIMEN (HYSTERESIS EFFECT); THE PERMEABILITY DEPENDS ON THE MAGNETIC FIELD, AND CAN REACH VALUES OF THE ORDER OF 10E+06 TIMES THAT OF FREE SPACE; ABOVE THE CURIE POINT, THESE MATERIAL BECOME PARAMAGNETIC.

ANTIFERROMAGNETIC: THOSE IN WHICH THE MAGNETIC MOMENTS OF ATOMS OR IONS TEND TO ASSUME AN ORDERED ARRANGEMENT IN ZERO APPLIED FIELD, SUCH THAT THE VECTOR SUM OF THE MOMENTS IS ZERO, BELOW A CHARACTERISTIC TEMPERATURE CALLED THE NEÉL POINT; THE PERMEABILITY OF ANTIFERROMAGNETIC MATERIALS IS COMPARABLE TO THAT OF PARAMAGNETIC MATERIALS; ABOVE THE NEÉL POINT, THESE MATERIALS BECOME PARAMAGNETIC; EXAMPLE: HEMATITE.

FERRIMAGNETIC: THOSE IN WHICH THE MAGNETIC MOMENTS OF ATOMS OR IONS TEND TO ASSUME AN ORDERED BUR NON-PARALLEL ARRANGEMENT IN ZERO APPLIED FIELD, BELOW THE NEÉL POINT; IN THE USUAL CASE, WITHIN A MAGNETIC DOMAIN, A SUBSTANTIAL NET MAGNETIZATION RESULTS FROM THE ANTI-PARALLEL ALIGNMENT OF NEIGHBORINGNON-EQUIVALENT SUBLATTICES.; THE MACROSCOPIC BEHAVIOUR IS SIMILAR TO THAT OF FERROMAGNETISM, ABOVE THE NEÉL POINT, THESE MATERIALS BECOME PARAMAGNETIC.

METAMAGNETIC: THOSE WHICH ARE ANTIFERROMAGNETIC IN WEAK FIELDS, BUT WHICH BECOME FERROMAGNETICALLY ORDERED IN STRONG APPLIED FIELDS.

Common **paramagnetic** minerals are **pyrite, markasite, rutile, dolomite, magnesite, beryll, dioptase;**
common **diamagnetic** substances are: **copper, gold, silver, bismuth, lead, sulphur, halite, fluorite, galena, quartz, calcite, apatite, topas, zircon** (only if very pure!);
the following known terrestrial minerals belong to the **ferromagnetic** group:

elements: **Fe, Co, Ni, Gd**

awaruite: Ni_3Fe (crystal lattice of Ni, ca. 78% Ni; common in serpentinites, e.g. Josephine Co., OR, Awarua, New Zealand);

wairauite: CoFe (common in serpentinites, e.g.: Wairau Valley, New Zealand);

magnetite: $Fe^{II}Fe^{III}_2O_4$;

magnoferrite: $MgFe_2O_4$;

jakobsite: $MnFe_2O_4$ (in limestones; heavily magnetic!);

franklinite: $(Zn, Mn^{II})(Fe^{III}, Mn^{III})_2O_4$ (marbles and skarns, e.g.: Franklin, NJ);

trevorite: $NiFe_2O_4$ (rare, e.g.: Barberton, Transvaal)

maghemite: γ-Fe_2O_3 (originate from magnetite, widespread, e.g.: Iron Mt., Shasta Co., CA, Bushveld, Transvaal, Sierra Mutum, Bolivia)

cubanite: $CuFe_2S_3$ (widespread, e.g.: Morro Velho, Brasil, Ellamar-District, Alaska, Otjosongati, Namibia, Kaveltorp & Tunaberg, Sweden);

Pyrrhotite: FeS (only monoclinal 4C-phase!, widespread, associated with pentlandite $(Ni, Fe)_9S_8$, especially in mafic rocks (gabbros/diorites, more rare: basaltoids), in pegmatitic-pneumatolytic dykes (e.g.: Tysfjord, Norway, Tunaberg, Sweden), in hydrothermal dykes (e.g.: Morro Velho, Brasil), in both, contactmetamorphic aureoles and regionalmetamorphic terraines (e.g.: Bajuvarian Forest, W-Germany, CSSR, Ducktown, TN, common to the Baltic Shield), in sedimentary rocks (rare, e.g.: Crimea, USSR).

In mineral separation we use the **mass-susceptibility** (S), which is given by:

$$S = \{[(\mu-1)/(4\pi\varrho_M)]\ E+06\};\ [cm^3g^{-1}] \quad (1)$$

ϱ_M: specific density of a mineral;

μ: magnetic permeability of a mineral.

heavily magnetic minerals: S = > 35,000 E+06 cm^3g^{-1};
normally magnetic minerals: S = 7,500 - 35,000 E+06 cm^3g^{-1};
weakly magnetic minerals: S = 200 - 7,500 E+06 cm^3g^{-1};
non-magnetic minerals: S = < 200 E+06 cm^3g^{-1}.

In general terms, the grouping of either ferro-, para- or diamagnetic elements in the structure of a mineral will influence its permeability. Since elements of all six different magnetic types may be present, a given mineral will not necessarily be either para-, dia- or ferromagnetic. Para- and ferromagnetic minerals are attracted when placed in a magnetic field, a property used by the Frantz isodynamic separator. This property is less sensitive to chemical variations than is density, but extremely clean separations can be made only with certain minerals.

A magnetic separation is only possible applying an inhomogeneous, isodynamic field, where translatory forces are produced. In a homogeneous field the inserted minerals are only affected by a moment of rotation and subsequently oriented parallel to the direction of the magnetic field, without any further movement. A field is called isodynamic, if at any given point the product of induction-constant (μ_o), field-strength (H) and the change of the fieldstrenght (grad H) at a given point of the vector-field in the direction normal to the equipotential-planes (on the side of decreasing H-values) equals constant:

$$\mu_o * H * \text{grad } H = \text{const} \qquad (2)$$

3. GENERAL REMARKS ON THE FRANTZ ISODYNAMIC SEPARATOR:

The separator consists of an **electromagnet** with a slot between its pole shoes. A **chute** made of non-magnetic material is mounted in this slot which can be set vibrating at an controllable amplitude. The whole magnetic system can be moved around two axes, whereby the direction at right angles to the length of the chute will be called **side slope**, and parallel to the length, **forward slope**. The minerals to be seperated are inserted into the system by means of a funnel.

The shape of the pole shoes is calculated to fulfill equation (2). Therefore the magnetic force F_m effecting a mineral grain is given

by:

$$F_m = C * X * I^2 * V \quad (3)$$

I: exciter amperage;
C: constant;
X: susceptibility;
V: volume of mineral grain.

The side slope β results in a gravity component G'

$$G' = \gamma * V * g * \cos \beta \quad (4)$$

g: weight of the mineral grain;
γ: conductivity;
directed opposite to the magnetic force. If $G' > F_m$, the mineral grains move to the lower side of the chute, if $G'' < F_m$ the resulting movement is directed vice versa. **At a given side slope β and exciter amperage the classification of mineral grains along the chute is dependent only upon their specific susceptibility!**

At its lower end the chute is divided by a center rail, so two different susceptibility classes can be extracted into two beakers. **By systematic change of the exciter amperage, a mixture of different mineral grains can be split into different susceptibility-classes!**

Therefore the most important settings are **side slope Ã and exciter amperage**! Both, forward slope and vibration amplitude define only the transport velocity within the chute and the time of separation respectively.

4. SOME IMPORTANT FACTS BEFORE GETTING STARTED:

a. **Under all circumstances, stay away from the separator when carrying a CARDIAC-PACEMAKER** - otherwise this might have been the last work you tried to perform! You also might not want to carry a **hearing-aid**, since interference of this device with the strong electromagnetic field generated by the separator might cause severe **damage to your inner ear!**

b. **Do not carry a watch** - this might cause the sudden "death" of your precious jewel or at least will not be very much appreciated by its electronics! Also, remember: You are dealing with a very strong electromagnet: You therefore **do not want to use screwdrivers, spatulas, pocketknifes or similar tools close to the pole shoes** - because those will be just as fast as strongly attracted by the magnet!

----------AVOID INJURIES OR DAMAGE TO EQUIPMENT!----------

c. Make repeatedly sure that the funnel is screwed in tightly and not became loose by the oscillation of the chute! Do not overfill the funnel - since very fine-grained materials behave almost like Newtonian fluids, they tend to spill!

d. Make sure **ahead** of any separation that **no ferromagnetic** or **strongly paramagnetic materials** are left clinging to the chute or pole shoes. You might rather want to clean the apparatus (using a fine paint-brush!) again, instead of spoiling your sample!

e. **Remove all ferromagnetic minerals and particles** (abrasive from former crushing, grinding!) **before loading the sample** into the separator (using the method described further below!). Even very few of those particles will positively block the chute and will lead to spill, requiring clean-up and to repeat the separation (think of your precious time!), and might even cause loss of your sample!

f. Make sure your samples are not contaminated with dust, lints or oversized mineral grains! Dust causes static charge, lints and oversized grains blockage of the funnel - both worsen seriously the results of your separation!

g. **Do not leave the separator unattended or let it run without load!** The effectiveness of your work is highly dependent upon continouity - i.e. the separation will be achieved most in the highest quality if you stay with the separator while running and add material constantly! Remember: The throughput of your sample is not only dependent upon forward slope and exciter amperage, but also upon content of higher paramagnetic minerals!

h. Normally a **side slope** of approximately **20°** is used and a forward slope near **30°**. A steeper forward slope may cause the grains to bounce when coarser grain sizes are being separated whereas too small a slope with finer grain sizes will impede free flow of the sample down the chute. Smaller side slopes (2° - 10°) are used to separate the minerals with very small magnetic susceptibilities which would separate on the non-magnetic side of the chute at a 20° slope and maximum current. However, while standard settings of 20° side slope and 30° forward slope are normally used, these values are not at all critical. Many laboratories use 10° to 15° side slopes and smaller forward slopes. So any satisfactory setting can easily be determined by "trial & error" - feel encouraged to try on your own settings!

i. Rate of flow is controlled by screwing the input funnel up or down. Similarly a steeper forward slope will increase rate of flow or a gentler slope decrease it. The proper rate of flow can be judged by eye after a little practice. Usually, given the slopes suggested, a flow rate of $+/-1cm^3min^{-1}$ will result. However, rapid initial separations such as the removal of 90% quartz + feldspar from a rock in which it is desired to concentrate a magnetic mineral present in small amount, can be made at a rate of $+/-5cm^3min^{-1}$. Final purification of the desired mineral would than be made at perhaps $0.3cm^3min^{-1}$. But you should remember that fine powders will flow at somewhat lower rates and coarser at faster. The thickness of the stream of powder should be kept always the same. Once having observed the proper stream thickness, there is no difficulty in adjusting the flow for any grain size or slope to conform to this optimum stream thickness.

j. In general the sample should be at least roughly sized. Ordinarily separations are made in the range **63μm - 180μm** (DIN 4188), or **230mesh - 80mesh** (ASTM E11-70) respectively. **500μm (30mesh)** is about the largest size on which separations are convenient and **45μm (325mesh)** about the smallest. With

the finer sizes difficulties may be encountered from electrostatic charge on the particles and consequent "balling up". If, however, the sample can be disaggregated, good separations can be made down to 45µm or 325mesh respectively.

k. **Do not forget to CLEAN the whole apparatus as well as eveything else used during your operation IMMEDIATELY after use!** That prevents not only spoiling your samples but will be greatly appreciated by the next user!
For cleaning of the magnet, especially the pole shoes and the chute, use **carbon tetrachloride** preferably. It is important that **no OIL** or any cleaning material containing **GRAESE** should be used under any circumstances on these parts, since even a thin film of oil/grease will cause grains to stick and either impair the separation or cause cutting of the sliding parts.

l. Report all accidents or damage to equipment immediately - so it can be taken care of!

4. HOW TO USE THE FRANTZ ISODYNAMIC SEPARATOR

----(ALWAYS START WITH A. BEFORE PROCEEDING TO ANY OTHER STEP!)---

A. Preparation of samples:

a. Use the binocular first to find out about grain sizes and compounds in your sample;

b. prepare a fraction between 63µm and 180µm or 230mesh to 80mesh respectively, by sieving (for restrictions on grain sizes see above!);

c. wash your sieved sample using ethanol/methanol or acetone; do **not use destilled water to avoid staining of the grains** by iron oxide produced from iron filings; this may most easily be done by stirring the sample in a beaker of solvent, allowing it to settle for 20s and decanting the solvent several times, or by scrubbing it in an ultrasonic cleaner; dry samples; **(wash and dry samples in proper ventilated hood only! Do not use infrared lamps in mineral separation lab to dry samples previously washed with organic solvents!);**

d. use binocular again - if still heavily contaminated with dust or lints (remember: If the grains are dust-coated, the quality of the separation may be materially reduced!): Repeat step c. (decide which type of minerals you need to separate and for what purpose: You might find it suitable to use diluted acids (HNO_3, HCl) for further cleaning. If you do so, you have to wash the sample several times using aqua dest. afterwards! Remember: This might result in staining, so you might find it worth to remove iron filings with a paper-wrapped hand-magnet first!); if only few contaminants remain, use hand-picking for final clean-up;

e. try to make sure that maximum grain size is smaller than intergrown particles - otherwise extract intergrowths by either milling to finer grain sizes or sieving using finer maximum sieve-size. If you had to go through this, repeat c. and d.!

B. Fast separation of ferromagnetic particles and contaminants:

a. Take chute out of pole shoes;

b. turn (using both hands) magnet so direction of slot is vertical;

c. cover whole length of slot with paper and fix it to the pole shoes using Scotch™ (or whatever else suitable) - DO NOT LEAVE ANY PART OF THE POLE SHOES UNCOVERED!!! (this positively will result in a lot of trouble for you!);

d. switch on low exciter amperage (0.1 A is definitely sufficient!);

e. put a wide porcelain/glass/aluminum (NO STEEL PLEASE!!! Remember, you are dealing with a magnet...) beaker underneath the end of the slot;

f. build yourself a funnel using thick aluminum/plastic foil or paper and form the outlet so it matches the shape of the slot (you might as well use a plastic funnel for more permanent use; however, to avoid cross-contamination of different samples, you better build a new one every time!);

g. let the sample fall freely and at good pace through the slot into the beaker;

RESULT: Ferromagnetic particles or contaminants stick to the paper, so the sample will be freed of them almost quantitatively at the first run.

h. Take another beaker - switch off amperage and all this ferromagnetic stuff is going to fall into this beaker.

SUGGESTION: Do not mix up beakers.... (it happened to me several times!). Repeat this procedure at least two more times to yield good results; if you feel you already did a good job on that and "anyway you are short of time..." - you might regret not having followed this advice, but will be convinced (same as I was first doing this!) not to skip it the next time!

----------CLEAN THE FRANTZ COMPLETELY!----------

C. Fast separation of diamagnetic minerals:

a. Take the chute out of the slot;

b. adjust forward slope to about 85°, side slope to about 2°-5°;

c. insert funnel (see above!) into slot facing toward you;

d. design a "sample-separating device" (carton, cardboard) and mount to lower end of slot;

e. provide two beakers underneath outlet separated by this carton;

e. switch on **high** exciter amperage (at least 1.2 A);

f. insert sample like during B.

RESULT: Only diamagnetic grains will not be deflected and fall straight downwards into the provided beaker (the one closer to you).

g. Remove beaker with diamagnetic grains and switch off magnet - all paramagnetic grains will now fall into beaker left.

SUGGESTIONS: Build "sample-separating-device" in a manner, that you are able to insert a "separating wall" about 1" into slot. Repeat this procedure several times - and do not mix up with your beakers.....

ADVANTAGE: This separation is highly recommended for greater sample volumes (up to 20kg/day) of rocks containing great amounts of diamagnetic minerals like quartz, feldspars,

calcite - e.g.: sandstones, quartzites, quartz veins, aplites, limestones, mables etc.

----------CLEAN THE FRANTZ COMPLETELY!----------

D. **Removal of small amounts of diamagnetic minerals from huge amounts of paramagnetic grains:**

a. Leave chute in place;

b. adjust forward slope to 20° - 30°, side slope to 2° - 3° **facing forwards** (instead of backwards as usual!);

c. hang both aluminum beakers into hooks at end of chute;

d. adjust exciter amperage to **at least 1.2 A**;

e. insert sample through funnel mounted to chute, adjust rate of flow by screwing the input funnel up or down, look for constant flow rate, prevent spilling;

RESULT: Diamagnetic minerals will be collected in the beaker facing to you, paramagnetic minerals will be deflected into the rear beaker.

ADVANTAGES: Method provides purification especially for **biotite-, amphibole-, pyroxene- (omphacite!) pre-concentrates.**

----------CLEAN THE FRANTZ COMPLETELY!----------

E. **Separation of a mineral mixture into "magnetic" and "non-magnetic" fractions:**

a. Adjust side slope to 10° (facing backwards!), forward slope to 20°;

b. choose medium oscillation of chute;

c. set exciter amperage to 0.1A;

d. insert approximately 1cm³ of sample into funnel and let completely "separate";

e. switch off oscillation and view both fractions yielded under binocular - there are three possibilities:

   1. all minerals present are to find in both beakers - there has been virtually **no separation** taken place;
   2. there are some mineral species enriched in the magnetic and non-magnetic separates respectively - but **no quantitative separation** has taken place;

3. the magnetic fraction consists of one or more mineral species, which do not occur in the non-magnetic fraction anymore - **complete separation** was achieved.

In cases 1. and 2. return **both** fractions to funnel, in case 3. only **non-magnetic** fraction;

f. increase exciter amperage **slightly:**

case 1.: appr. 0.05A;

case 2.: appr. 0.1A;

case 3.: appr. 0.2A;

switch oscillation of chute on;

proceed with step d. until your sample has been separated into as many fractions obtainable by this method.

RESULT: This is the most complete separation possible using the Frantz isodynamic separator!

----------CLEAN THE FRANTZ COMPLETELY!----------

5. GENERAL COMMENTS:

Even so the Frantz isodynamic separator is a powerful tool in separating minerals one might often encounter mineral species having fairly similar susceptibilities. In this case even the most careful variation of both slopes, flow rate and exciter amperage will not lead to a satisfying result.

Previous experience has shown that especially slowly cooled minerals of plutonic rocks often do not exhibit a scatter in susceptibilities sufficient for using this method. However, metamorphic, sedimentary and volcanic rocks generally display far greater variation and thus are more apt for applying the Frantz.

Empirical studies have yielded the following table for para- and diamagnetic minerals:

a. magnetic fraction at side slope 20°:

0.4 A:	0.9 A:	1.2 A:
ilmenite	hornblende	diopside
garnet	hypersthene	tremolite
olivine	augite	enstatite
chromite	aktinolite	spinel
chloritoid	staurolite	muscovite
hematite	epidote	zoisite
	biotite	clinozoisite
	chlorite	turmaline
	"schörl"	

b. side slope: 5°; amperage 1.2 A:

magnetic fraction:	non-magnetic fraction:
titanite	zircon
leucoxene	rutile
apatite	anatase
andalusite	brookite
monazite	pyrite
xenotime	corundum
	topaz
	fluorite
	kyanite
	sillimanite
	anhydrite
	beryl
	diamond

III. THE USE OF HEAVY LIQUIDS

1. INTRODUCTION:

The separation of mixtures of mineral grains according to their specific density using "heavy liquids" has been used since almost a 100 years. Density is one of the most sensitive properties that can be utilized in mineral separations. Densities up to about $5gcm^{-3}$ can be obtained with heavy liquids. In general the separation is made by a **"sink-float" fractionation.** However, minerals with densitites over $5gcm^{-3}$ may be separated by panning or jigging - techniques which use water and eccentric motions to remove the lighter fractions.

Some introductory remarks should also be made regarding the heavy liquids, you may use: KRUMBEIN & PETTIJOHN suggested already in 1938 that a heavy liquid should have the following attributes to be effective: (i) inexpensive, (ii) easily prepared or purchased, (iii) transparent, (iv) liquid at ordinary temperatures, (v) non-corrosive, (vi) chemically inert towards most minerals, (vii) without odor, (viii) fluid, not viscous, (ix) easily diluted and recovered, and - one should add - (x) non-toxic. However, **none** of the heavy liquids now in use have all of these qualities, but some are better than others. Furthermore, there is a tendency of the expense of the liquids being directly proportional to their density. So, in any case, and besides what will be noted further down, all efforts should be made not only to gain the highest quality of separation of your sample, but to recover the liquids for re-use.

2. FUNDAMENTALS:

Specific density is a characteristic property of every solid or fluid at given pressure and temperature. Using heavy liquids to separate different minerals according to their specific density, the settling rate in a Newtonian liquid is given by STOKE's law:

$$v = [2gr^2(\varrho_c - \varrho_L)]/(9\eta) \quad (5)$$

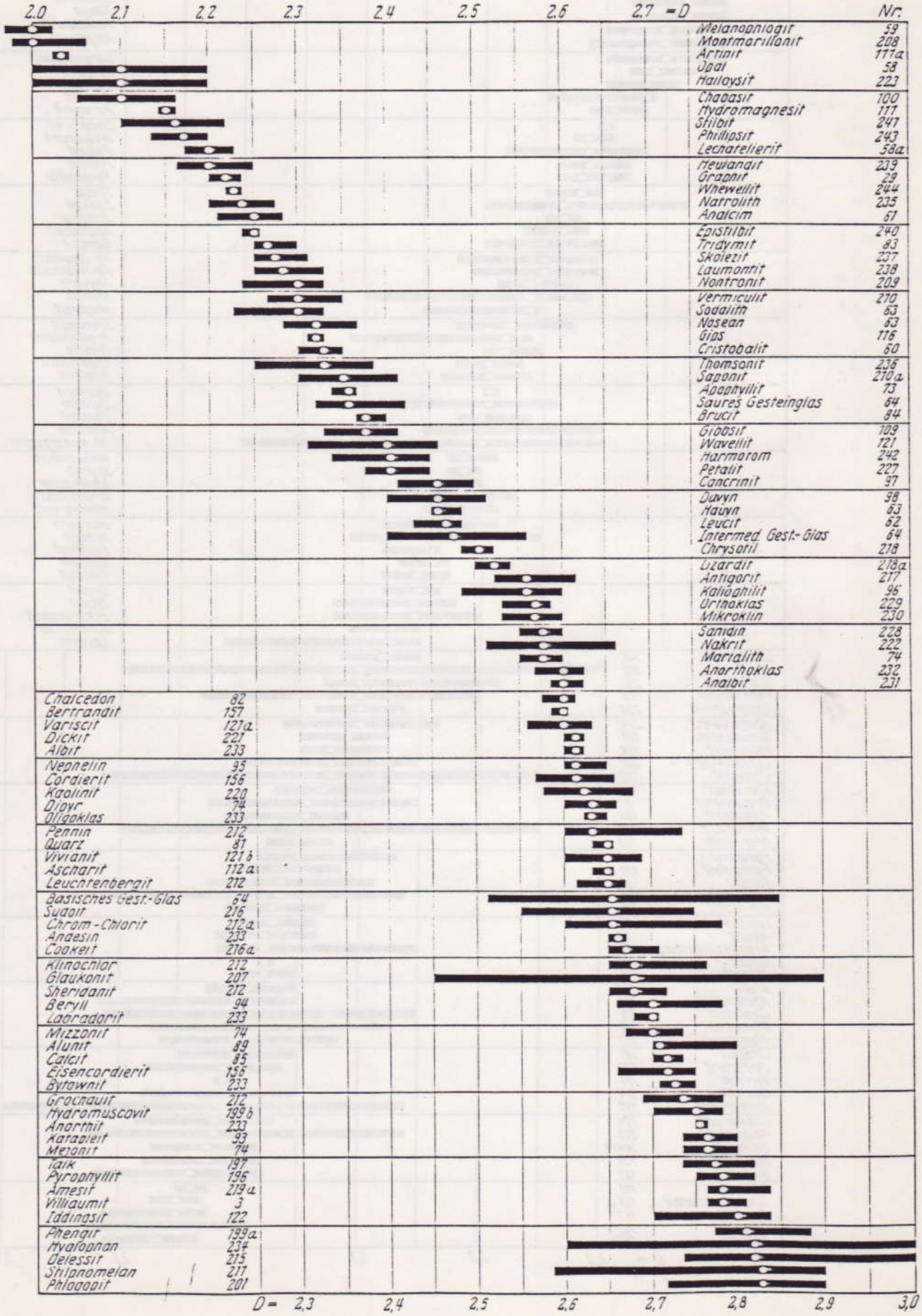
g: gravity acceleration;
r: radius of a spherical crystal
ϱ_c , ϱ_L: density of the crystal and the liquid respectively
η: viscosity

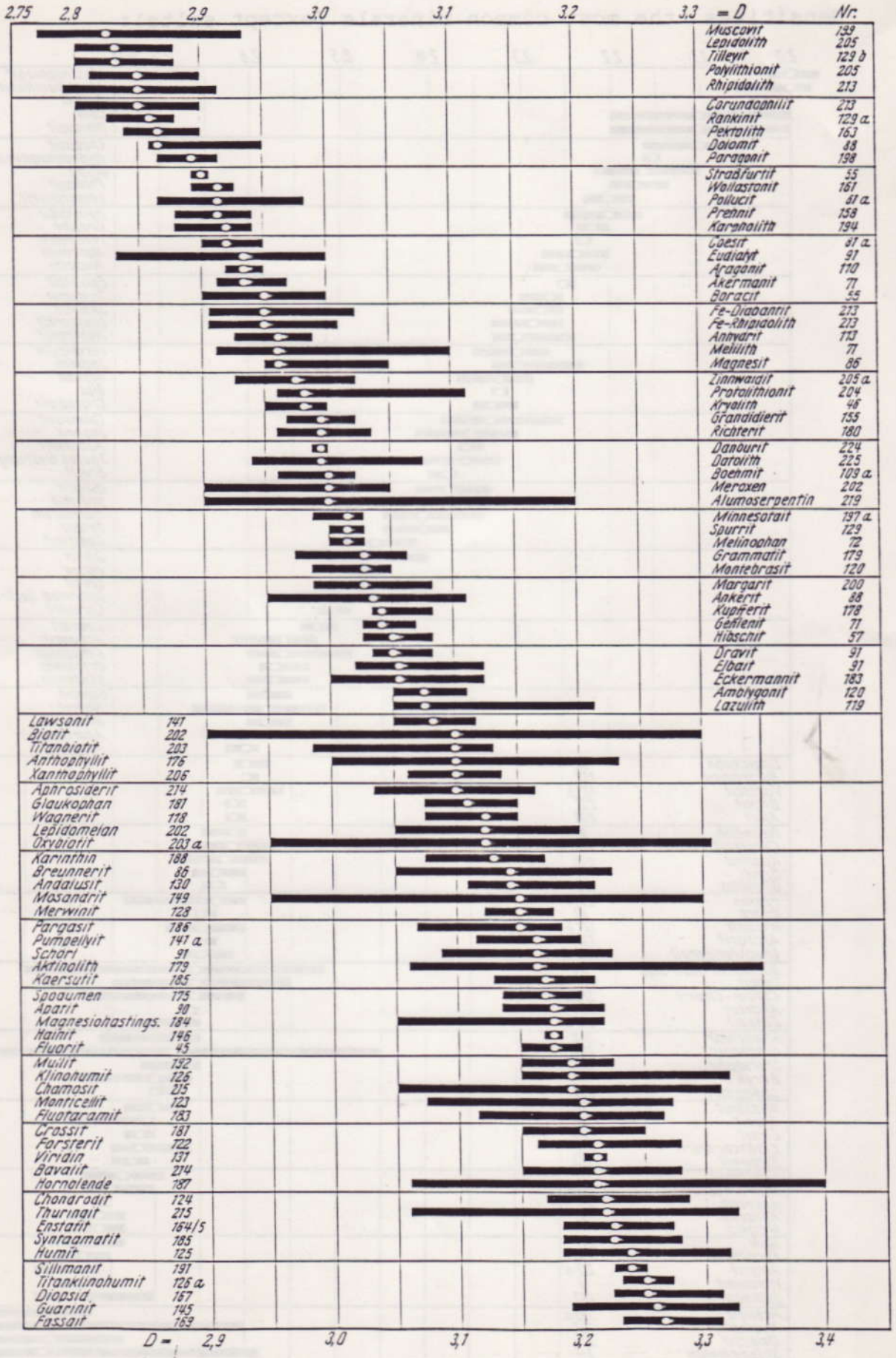
The density of minerals, however, might be widely variable due to several reasons:

a. by far the majority of rock-forming minerals are solid-solutions, so their compositions might be widely variable mixtures of up to four major components;
b. specific lattice components might be substituted by heavier or lighter ones;
c. part of the hydrous phases might be removed from crystal lattice;
d. minerals might exhibit intergrowth with other minerals or fluid/gaseous inclusions which due to size cannot be separated;
e. minerals containing U and/or Th might show a tendency to isotropisation and thus decrease in density; the specific density of these minerals (e.g.: zircon, monazite) can vary fairly widely.

Density ranges of the most common minerals are given in the following table (TROEGER, 1971):

Densitites the most common minerals (except salts):

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Lepidolith 205
Tilleyit 129 b
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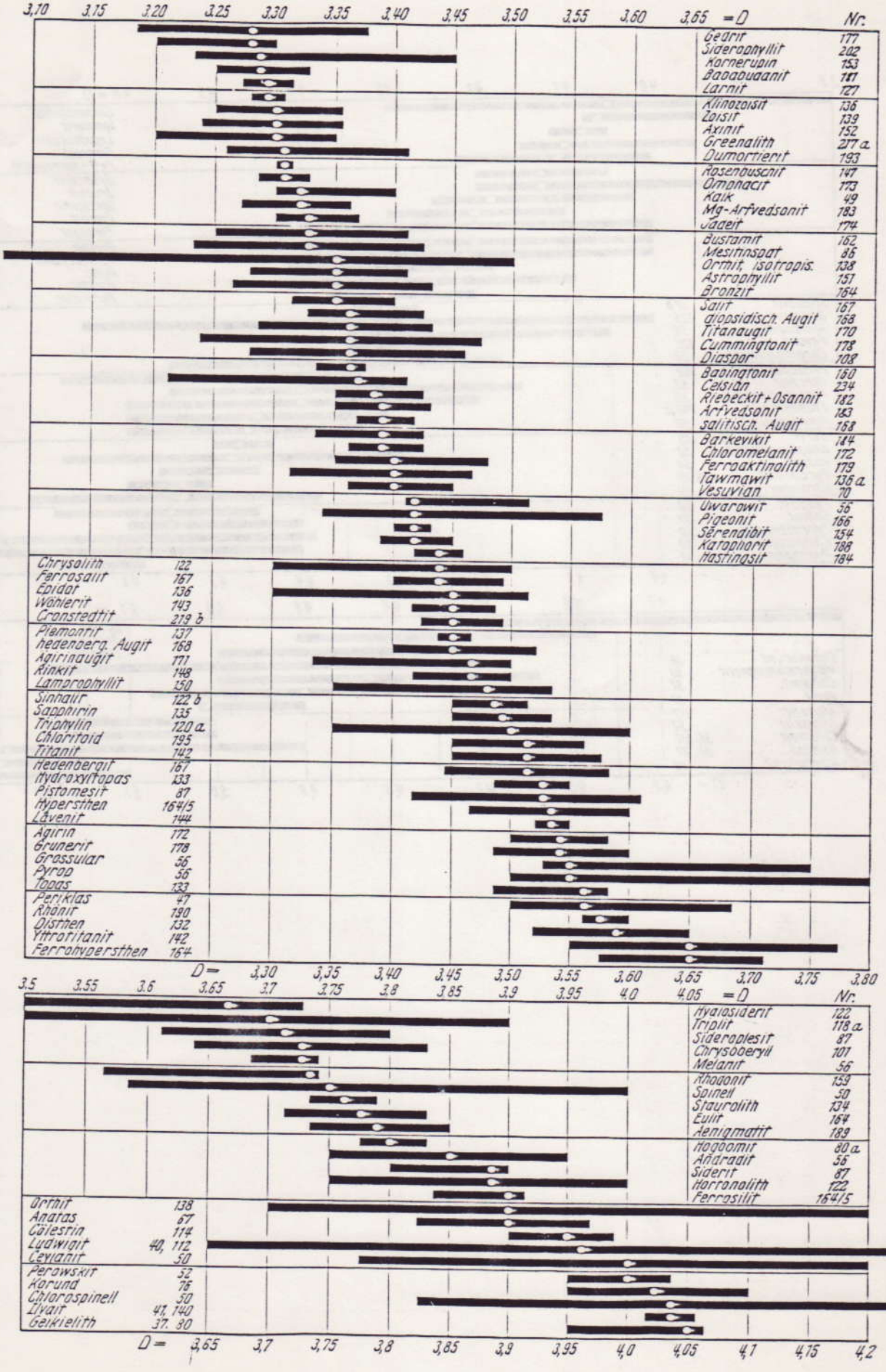
3,10 3,15 3,20 3,25 3,30 3,35 3,40 3,45 3,50 3,55 3,60 3,65 = D
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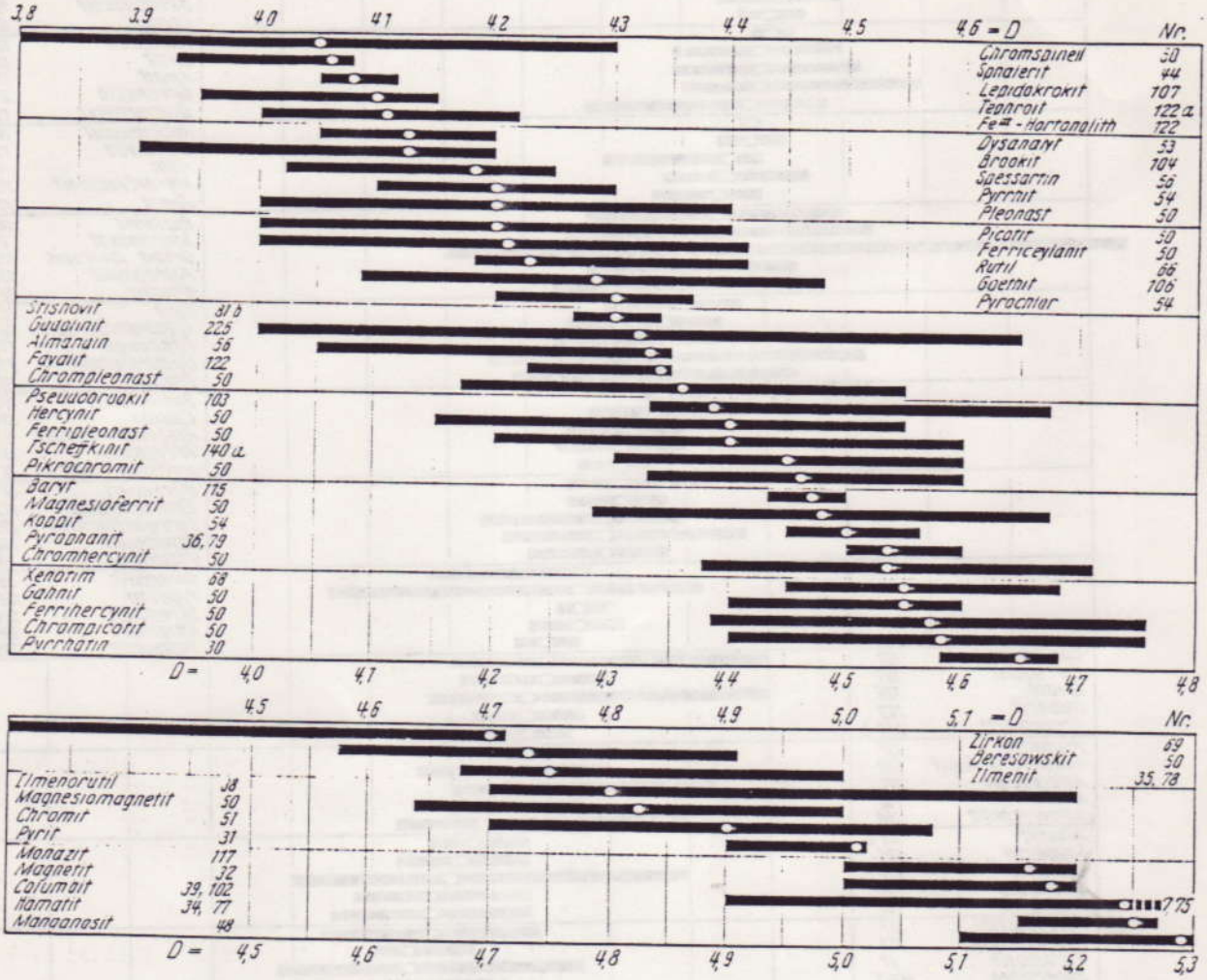
3,8 3,9 4,0 4,1 4,2 4,3 4,4 4,5 4,6 = D Nr.
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D = 4,5 4,6 4,7 4,8 4,9 5,0 5,1 5,2 5,3

Most critical - besides that the actual density of a particular mineral can just be estimated - is the grain size of the sample: Density separation using heavy liquids is virtually **not possible** for grain sizes <36 m (<400mesh) - unless one uses a centrifuge! The fine material has a tendency to clot with the heavies dragging down some lights and the lights will occlude some of the heavies. Similarly, the minimum sample volume recommended - given the apparatus used - should not fall below $1cm^3$. On the other hand, it is possible to fractionate minerals having a difference in density of only E-02 gcm^{-3} - even so this requires painstaking work.

3. HEAVY LIQUIDS COMMONLY USED:

a. <u>Sodiumpolytungstate</u>, [$3Na_2WO_4.9WO_3.H_2O$], non-toxic, contains about 86.66% WO_3 and is readily soluble in water (up to 80 mass-% at 25°C; mass-% = (gram [substance]/gram [substance + water])*100). The maximum density of an aequous Na-polytungstate solution is 3.12gcm^{-3} (25°C), but can be extended by adding tungsten carbide powder to the saturated solution. The desity of this cloudy suspension will than reach up to 4.6gcm^{-3} (25°) by introducing up to 40% tungsten carbide. The aequous solutions are colourless, stable within a pH-range of 2-14 and are both, easy to prepare and regenerate.

For preparation and use of Na-polytungstate solutions, please note the following:

- **use only destilled water;**
- **use only glass containers;**

- if possible, do not allow the solution to come into contact with reducing agents. However, if it should, the resulting blue colour has no influence on the density chosen;
- the polytungstate solution should be recovered by washing respective particles with aqua dest. and then evaporating to the desired density, or adding solid polytungstate respectively. Do not use any organic solvents for washing!
- the sample material to be separated should be free of soluble Ca-components! Otherwise, insoluble Ca-polytungstate will be formed. A respective example are clay minerals; if in any doubt, please wash sample thoroughly in hot destilled water!
- two major disadvantages have to be remarked:
  - the viscosity of a Na-polytungstate solution increases very rapidly above a density of 2.5gcm^{-3};
  - Na-polytungstate has a rather high trace element content (Mo: +/-2ppm; As: +/-5ppm: U: +/-10ppm) that might interfere with chemical analysis of the concentrates if they are not cleaned carefully with aqua dest. to remove any residue.

For preparing solutions the following values are given for reference:

desired density of heavy liquid (gcm^{-3}):	Na-polytungstate to add: mass-%:	g (Na-polytungstate) / 1,0000ml aq. dest
3.1	80.00	4,000.00
3.0	77.50	3,450.00
2.9	76.25	3,210.00
2.8	75.00	3,000.00
2.5	70.00	2,300.00

b. **Bromoform**, [$CHBr_3$], maximum density: 2.894gcm^{-3} at 20°C, sensitive to light (should be stored in amber bottles containing copper filings or mesh), **metabolic poison**,

inhalation of small amounts causes irritation, provoking the flow of tears and saliva, reddening of the face, more serious exposure causes lacrimation and narcosis, can seriously damage the liver and cause death.

c. Tetrabromethan (acetylentetrabromide, Muthmann's solution), [$CHBr_2.CHBr_2$], maximum density: 2.967gcm^{-3} at 20°C, sensitive to light (should be stored in amber bottles containing copper filings or mesh!), cancerogene.

d. Methylene iodide (diiodomethan), [CH_2I_2], maximum density 3.325gcm^{-3} at 20°C, sensitive to light (should be stored in amber bottles containing copper filings or mesh!), decomposition products can seriously damage the nervous system and cause derangement of the vision, absence of conjunctival reflexes, pulmonary edema, blepharitis, opacity of the cornea and fatal effects from overexposure;

e. Thoulet's solution, aequous solution of potassium tetraiodomercurate-II [$K_2(HgJ_4)$], maximum density 3.155gcm^{-3} at 20°C, highly toxic mercury compound;

f. Rohrbach's solution, aequous solution of barium tetraiodomercurate-II [$Ba(HgJ_4)$], maximum density 3.485gcm^{-3} at 20°C, highly toxic mercury compound;

g. Clerici solution, equimolare solution of thallium formate [$TlHCO_2$] and thallium malonate [$Tl_2C_3H_2O_4$], maximum densities: 4.04gcm^{-3}/20°C; 4.60gcm^{-3}/90°C; 5.10gcm^{-3}/100°C, poisonous because thallium is in such a form it can be assimilated into the body (0.4g/kg body weight [7ml considering an average weight of 80kg!] are considered lethal!), Tl resembles Pb in its toxic properties and in that it is a cumulative poison, intoxication causes loss of hair, cramps, pains in the limbs with paralysis, diarrhea, nephritis, cardiac degeneration and ultimately death, Clerici causes skin irritations such as erythemas and rashes;
CLERICI MIGHT BE CONSIDERED THE MOST DANGEROUS OF ALL HEAVY LIQUIDS! Thallium compounds in solution are readily absorbed through the skin and from the digestive tract causing the toxic symptoms noted above. Clerici will cause almost instant

white coloration (later turning into a shiny, metallic silvery-grey!) on contact with the skin.

General remarks:

With the exception of the non-volatile aequous solutions (Na-polytungstate, Thoulet's-, Rohrbach's- and Clerici-solution), none of the above described heavy liquids might be used outside a properly ventilated fume hood (i.e. THEIR USE IS DEFINITELY PROHIBITED IN THE NEW MINERAL SEPARATION LABORATORY!)! This also affects the use of acetone in the laboratory! Since vapors of organic heavy liquids are heavier than air, hood has to be provided with a bottom ventilation!

Every person working with heavy liquids should take adequate safety precautions. These include:

- avoid prolonged contact with these materials;
- always wear disposable safety gloves while working with Clerici; in case of even the slightest contact with your skin, wash thoroughly with lots of detergent; watch for above described reaction (see physician immediately if reaction occurs - remember: A few mg might already be "enough"...!);
- wash your hands frequently when using the solutions;
- eating/drinking or storing lunches/beverages in the laboratory and near solutions is positively prohibited;
- clean the area you worked in and all apparatus immediately after use - the user next to you might not know, what you have been working with, - so, e.g. he most likely will not be aware of what is left in your glassware.....;
- dispose off properly - positively no heavy liquids or solvents in sewer;
- report all accidents or damage to equipment immediately.

BASED ON PREVIOUS EXPERIENCE, THE POTENTIAL DANGER OF THESE CHEMICALS AND ACCIDENT RATE, ANY PERSON NOT COMPLYING WITH THE ABOVE STATED RULES AND/OR ACTING WITH GROSS NEGLIGENCE SHOULD BE DEFINITELY SUSPENDED FROM THE USE OF THESE FACILITIES!

In case of intoxication: Remove foolhardy geologist to fresh air at once! If breathing has stopped (bromoform), use artificial respiration! Call ambulance immediately and make sure that label of solution used is provided for further information.

Minerals having ion-exchange properties (zeolith, smectite) react with anorganic heavy liquids, change their density and incorporate rather high amounts of heavy metals. Some sulfide minerals are decomposed by reaction with solutions containing heavy metals. Some organic solvents (acetone!) can be incorporated into clay minerals and cause decrease in density.

4. SEPARATION APPARATUS FOR USE WITH HEAVY LIQUIDS:

The simplest method for separation is the use of separatory funnels for mineral separation. The setup consists of:

a. the separatory funnel;
b. a dismountable filter funnel with a built-in ceramic filter membrane;
c. a filter flask, which can be evacuated by connection to a water-operated filter pump.

Both the heavy liquid used and the sample are introduced into the separatory funnel and agitated with a glass stirring rod. Dependent upon your grain size, density and viscosity of your heavy liquid you should not introduce more than a maximum of about 0.5cm of sample material; as a rule you should start with barely covering the surface of the heavy liquid with grains - wait and observe if the grains still settle freely, or start clotting to each other preventing separation. You may than (stepwise) add more material, stirring the mixture after each addition. Allow than the mixture to stand until the light and heavy fractions are completely separated. This might take quite some time, depending upon volume, density and viscosity of the heavy liquid. It is

advisable to agitate the lights several times to allow all the trapped heavies to sink.

Before proceeding, make sure a **filter** (preferably PTFE sieve-net or a fairly rapid laboratory grade filter paper (e.g.: Whatman #4); but a coffee filter will do nicely, especially since both, the wet strength of the coffee filter paper appears to be better and passing time is twice as fast than the laboratory grade filter papers - and they are about only $^{1}/_{10}$ the cost as e.g. Whatman #4 laboratory filters) **is inserted into the filter funnel** to prevent the ceramic membrane to get clogged by grain sizes <36µm (<400mesh). The heavies are than tapped off by turning the stopcock and allowing them to pass trough to the filter funnel. After the heavies are tapped, filter the liquids from the grains using the vacuum system. Than a **new** filter funnel (**do not forget to insert filter paper or PTFE sieve net!**) is introduced and the remaining liquid is tapped. Even so it is not essential, the filter process is best done under vacuum as this speeds the process and recovers a greater volume of the heavy liquid. After all the heavy liquid is recovered and returned to the stock bottle, the filter funnels containing both fractions are washed with destilled water or acetone. **To dry the samples do positively not use the IR-lamps**, when samples had been washed with **other solvent then destilled water** (mixtures of air and **acetone/methanol/ethanol** fumes are **explosive!**)! If acetone had been used - which is the safest (no staining!) and fastest (low boiling point) method - one **must use the fume hood** (or the oven) in the chemistry lab for drying! Furthermore, **do not contaminate heavy liquid solution with acetone or any other organic solvent** - always use destilled water only for cleaning of tapped samples unless filter flasks containing heavy liquid have been removed from filter funnels!

After each separation **one must thoroughly clean the whole apparatus:** Use destilled water first, than acetone (fume hood!),

allow to dry before next separation process! Never leave used glassware uncleaned as this will result in precipitation of Na-polytungstate on the walls and especially in the filter membrane, which might turn into insoluble Ca-polytungstates! Furthermore, turn the filter pump off, allow air to fill system and filter flasks, make sure IR-bulbs are switched off (timer!).

5. REMARKS:

The above-described method is not satisfactory for producing pure separates, particularly with fine material and is time-consuming. Furthermore, large volumes of liquid are needed with a resultant loss of more heavy liquid with each separation. However, the availability of comparably cheap, non-toxic Na-polytungstate, instead of the common, highly toxic heavy liquids, has greatly increased the use of this method. Centrifuging overcomes both of these difficulties, but the wide use of the centrifuge is not in evidence mainly because the special tubes and reinforced rotor axes needed have to be custom-built and are therefore expensive.