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AN INTRODUCTION TO

X-RAY DIFFRACTION ANALYSIS

AND

X-RAY FLUORESCENCE SPECTROCOPY

L.P. van Reeuwijk

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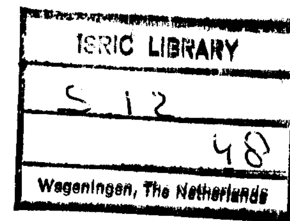
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AN INTRODUCTION

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by

Dr. L.P. van Reeuwyk

1990

Introduction

In soil analysis, two types of rather common instrumental techniques make use of X-rays. These are *X-ray diffraction* (XRD) for the identification and sometimes semi-quantitative determination of minerals, and *X-ray fluorescence spectroscopy* (XRFS) for the determination of the elemental or total chemical composition of materials. Since these techniques have several features in common, a discussion on the two can conveniently be combined.

The nature of X-rays

X-rays are part of the spectrum of electromagnetic radiation roughly in the wavelength range of 0.001 - 10 nm (0.01 - 100 Å). The position of this range in the spectrum is indicated in Fig. 1.

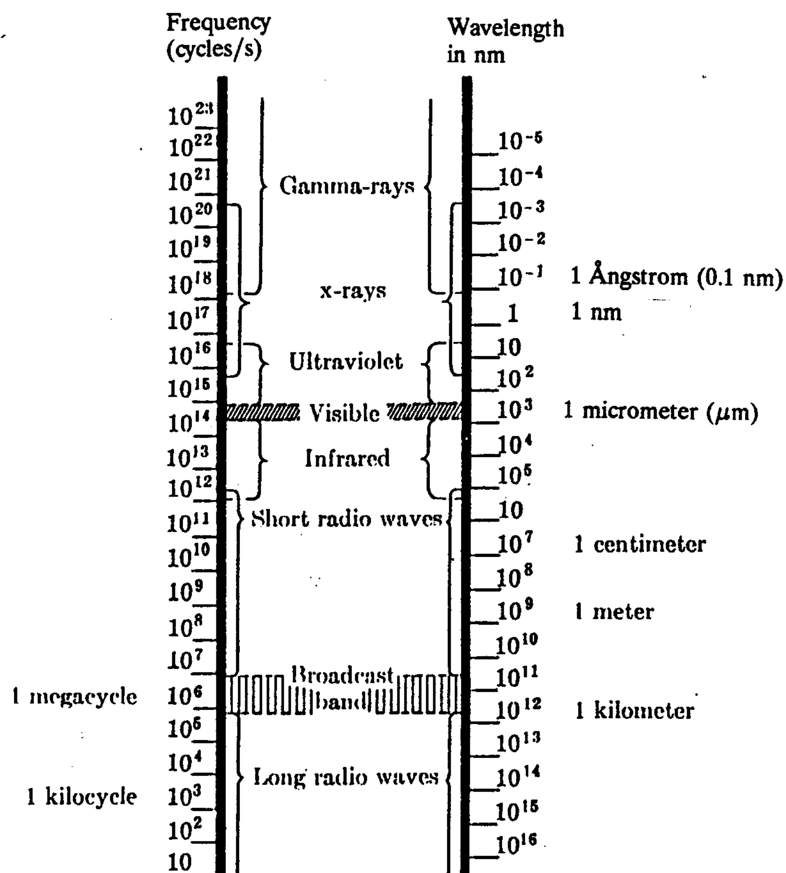

Fig. 1. The electromagnetic spectrum.

This shows that X-rays are situated between gamma rays on the short-wavelength side and ultraviolet rays on the long wavelength side, the boundaries not being well defined.

Because electromagnetic radiation can transfer energy and momentum by "bouncing" it has a dual nature in that it has properties of both waves and particles. Therefore, X-rays may also be considered as consisting of individual photons with an energy

$$E = h\nu = hc/\lambda$$

in which h is Planck's constant, ν is the frequency of the radiation, c is the velocity of radiation and λ the wavelength. When the constants are substituted the expression reads:

$$E = 12.4/\lambda$$

Thus there is a direct relationship between the energy of the photons and the wavelength: the shorter the wavelength, the higher the energy (the "harder" the X-rays).

The production of X-rays

X-rays are produced when a beam of electrons of sufficient energy strike any matter. The mechanism is shown in Fig. 2. The incoming (bombarding) electron 'knocks' an electron from its shell, upon which both electrons leave the atom.

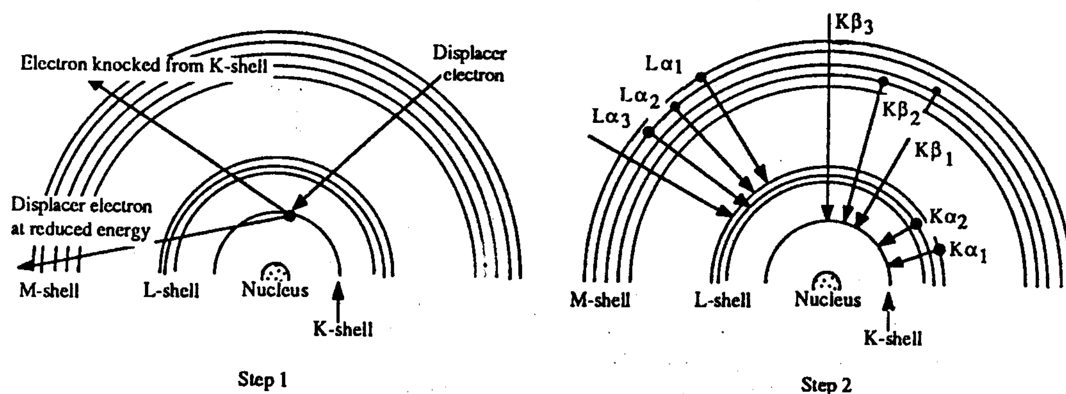

Fig. 2. Step 1 shows an electron being knocked from the K shell. The electron and the displaced electron, sometimes called a photoelectron, both leave the atom at a wavelength greater than that of the displacer electron as it came into the atom. Step 2 shows many of the possibilities for replacing displaced electrons. An X-ray photon is emitted when an electron "drops" from a higher level to refill a shell.

This, and the interaction with the crowd of other electrons they may meet, results in emission of radiation with a *continuous* spectrum of energies and wavelengths: the so-called 'white' or polychromatic or heterochromatic radiation or 'Bremsstrahlung' (brake-radiation). Electrons thus ejected leave vacancies behind that are immediately filled by electrons dropping in toward the nucleus from orbitals farther out. This is a "bang" to a lower level of energy and the energy E released through radiation depends on the original and new orbital and the kind of nucleus. This radiation is, therefore, *characteristic* for each element (i.e. with characteristic λ) . Some of the possible drops are also shown in Fig. 2.
X-rays of sufficient energy, in their turn, can also knock electrons out of their orbital. The resulting secondary X-rays caused by the dropping in of electrons are called "fluorescent" radiation and are characteristic for the irradiated atoms, identical to that caused by incident electrons.
The production of X-rays is a very inefficient process and only about 1% of the energy input is transformed into useful X-rays, the remainder being mainly transformed into heat which needs to be dissipated by forced cooling.

Practical application

In practice, X-rays are generated in an X-ray tube (see Fig. 3.). Electrons are emitted by a glowing tungsten filament (the cathode), pulled through the vacuum of the tube by a high voltage ranging from 15 to 60 kV and then strike a metal target (the anode). The sudden

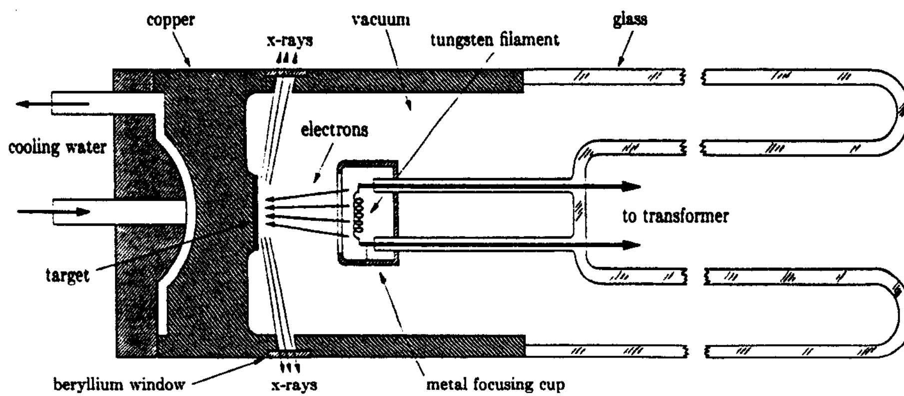

Fig. 3. Schematic section of an X-ray tube.

deceleration generates X-rays of the type as illustrated in Fig. 4. The bulge represents the continuous or white radiation on which is superimposed three characteristic wavelengths of, in this case, molybdenum. Monochromatic radiation (i.e. with one wavelength, usually K-α) is in practice obtained by using filters of thin metal foil or by a single crystal device. Detection of X-rays can be achieved in several ways but is mostly done with a kind of Geiger counter and, in X-ray diffraction, also by means of a photographic film.

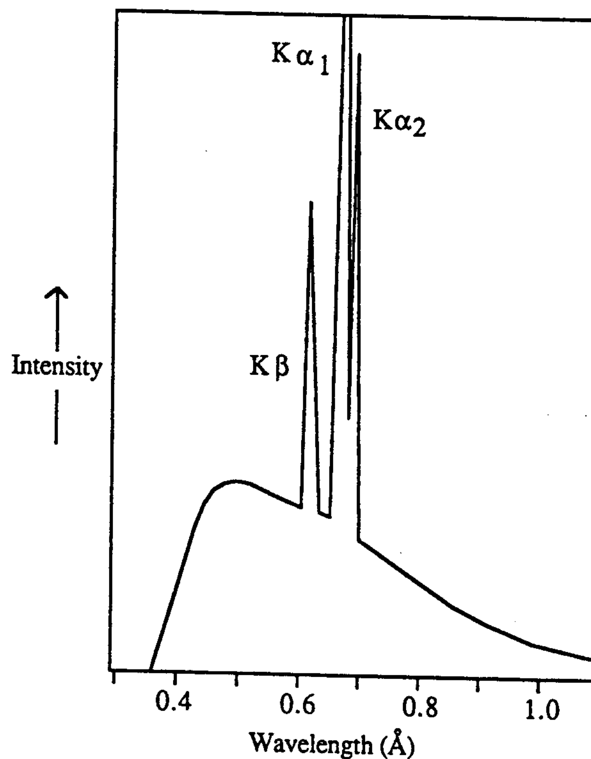

Fig. 4. Continuous radiation plus the characteristic radiation of molybdenum superimposed on it (voltage 30 kV).

Diffraction of X-rays

When X-rays encounter any form of matter, they are partly transmitted and partly absorbed. Absorption is effected in two distinct ways: by scattering and by true absorption. *True absorption* is caused by excitation and transition of electrons and may, as indicated above, result in fluorescent radiation.
Scattering occurs when the incident photons transfer their oscillation energy to electrons of the target atom which will then re-radiate the energy in all directions with the same wavelength as the incident beam (see fig. 5).

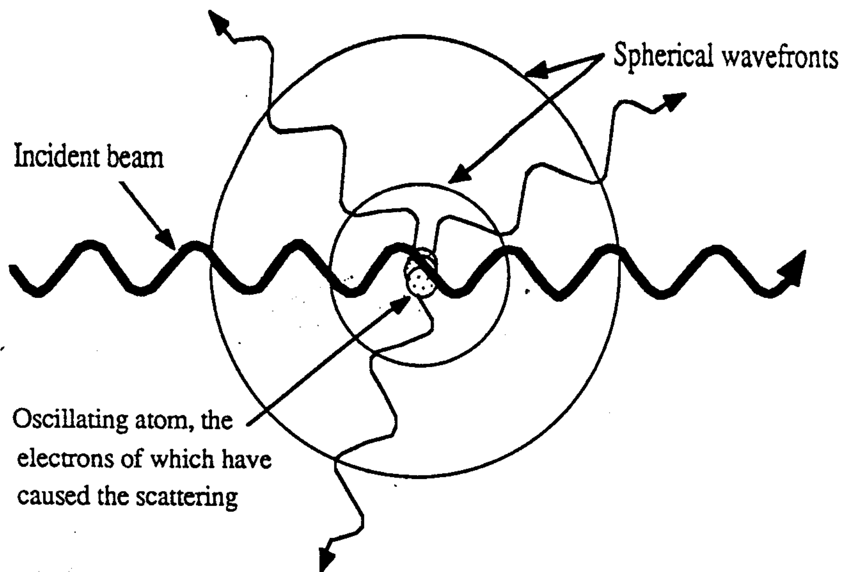

Fig. 5. An atom in the crystal structure behaving like a point source for radiation scattered in all directions.

Diffraction (or, less accurately, "reflection") of X-rays is effected by crystalline matter only and results from the mutual reinforcement of scattered rays when the waves become "in phase" under certain conditions. The conditions are the relative position of the waves and the crystal (angle of incidence) and the structure of the crystal itself. The structure of a crystal can be schematically illustrated as in Fig. 6. Crystals consist of atoms or ions located at fixed relative positions and which are always the same for each mineral species but

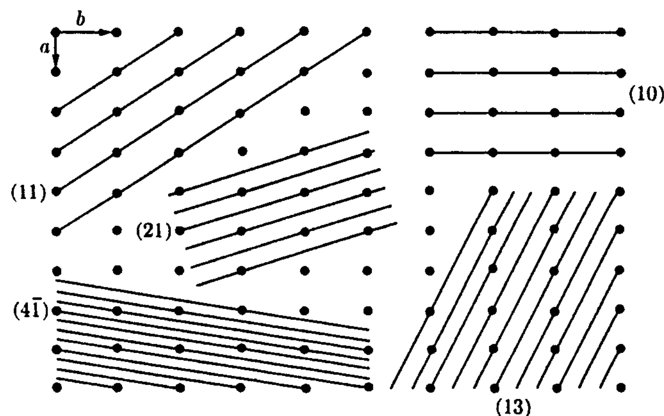

Fig. 6. Two-dimensional lattice, showing sets of crystal planes with different indices and spacings.

different for different species and constitutes the basis for identification. (In "amorphous" compounds, by contrast, atoms or ions are positioned at random without any periodicity or with only short-range order.)

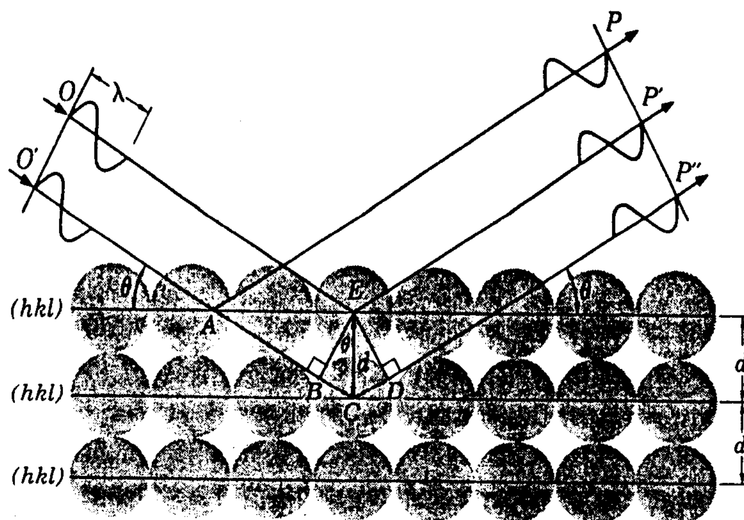

Fig. 7. Diffraction of X-rays by a crystal.

Of importance for diffraction is the existence of (sets of) parallel planes in which the atoms or ions are situated. This is illustrated in Fig. 7 which shows the conditions for diffraction The waves *O* and *O'* are incident X-rays diffracted by two planes of a set with indices (*hkl*) and a repeat distance *d* ("spacing"). It can easily be seen that rays *OEP'* and *O'AP* are *in phase* since their pathlengths between wavefronts *OO'* and *PP'* are equal.[1] The length of path of ray *O'CP"* is the distance *BC*+*CD* longer than that of the former rays. For mutual reinforcement (i.e. to be in phase with the others) this distance *BC*+*CD* should equal a whole number (1, 2, 3, etc.) of λ (wavelength).
If Θ is the angle of incidence (= angle of reflection) then $BC = CD = d\sin\Theta$ and hence

$$BC + CD = n\lambda = 2d\sin\Theta$$

This equation is known as Bragg's law. Other sets of planes in the crystal (with other values for *d*) will similarly diffract X-rays but at other angles Θ. X-ray diffractometry is the technique of recording such sheafs of diffracted X-rays. This is illustrated in the schematic drawing of a diffractometer in Fig. 8. The powdered[2] crystalline sample *C* diffracts the X-rays from tube *T* in those directions where Bragg's law is fulfilled. By scanning with detector D the angles Θ at which diffraction occurs can be

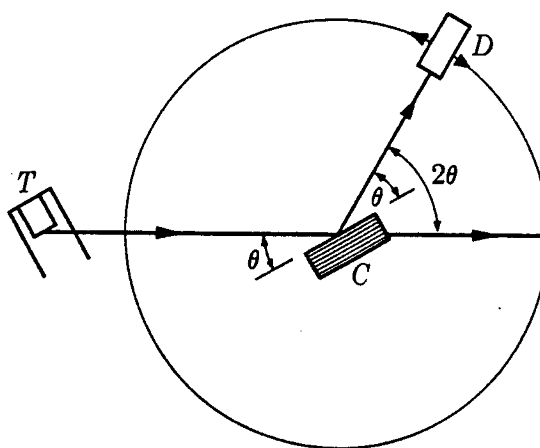

Fig. 8. Schematic drawing of a diffractometer (see text).

[1] Note that this always is the case at any angle of incidence, just like the reflection of light by a mirror, so that this diffraction by one plane contributes to the background "noise".

[2] The advantage of powdered over unpowdered material is that more crystal planes are in diffracting position at any time.

recorded[3] and thus the various values for *d* can be calculated with the aid of Bragg's law because the (monochromatic) wavelength λ of the used X-ray tube is known. In this way a "fingerprint" is obtained by which the mineral(s) can be identified. As mentioned earlier, recording of the fingerprint can also be achieved with a photographic film in an X-ray diffraction camera. A typical diffractogram is shown in Fig. 9. A complete diffractometer set-up is drawn in Fig. 10.

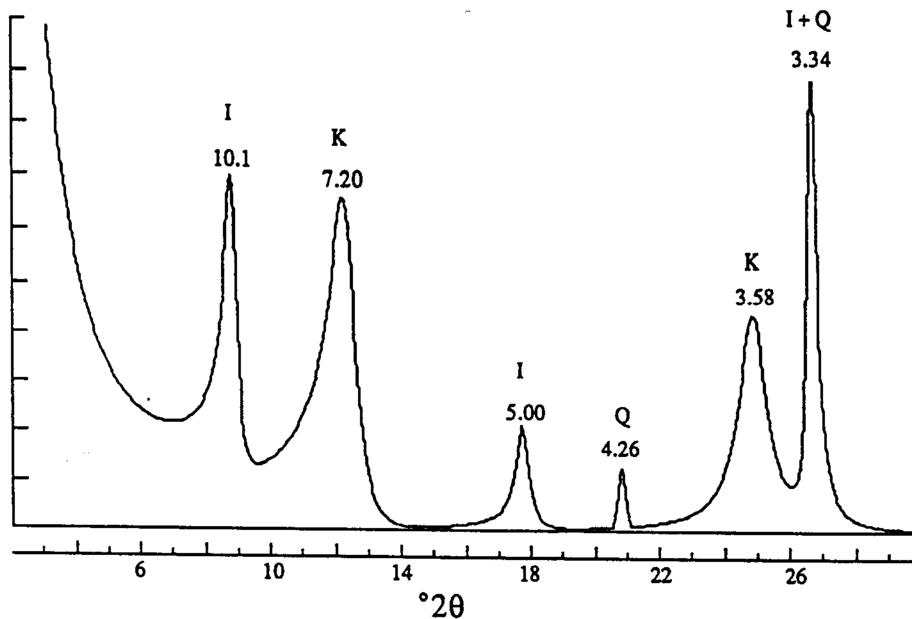

Fig. 9. Diffractogram of a mixture of illite, kaolinite and quartz.
(Figures above peaks are spacings *d* in Å)

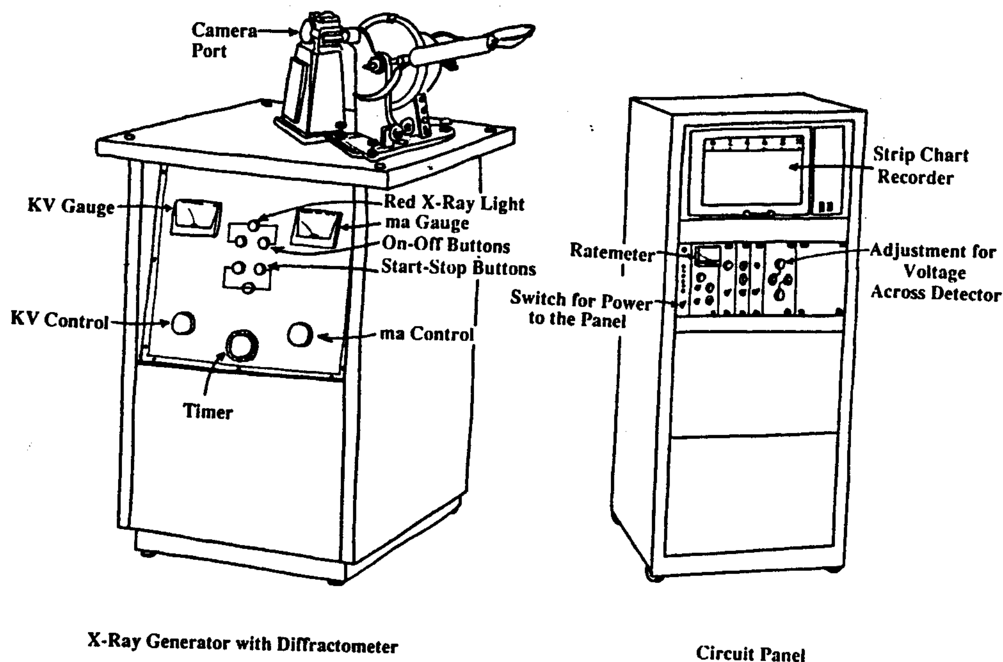

Fig. 10. Sketch of a Philips-Norelco X-ray diffractometer assembly.

[3] For a number of reasons such as focussing and higher reflection intensity, in diffractometers the sample carrier rotates with the detector (at half the angle-speed).

X-ray diffractometry is a *qualitative* method of analysis with semi-quantitative aspects in the form of relative diffraction intensities (peak height and peak area in diffractograms; degree of blackening on photos). The detection limit varies with the kind of mineral and degree of crystallization and is in the range of 2 - 5% (w/w).

X-ray fluorescence spectroscopy

In addition to diffracted X-rays, incident X-rays also produce secondary fluorescent radiation with wavelengths characteristic for the atoms in the struck material. A combination of these features can be put to good use in analysing the chemical composition of a sample. The principle of such a spectrometer is represented in Fig. 11. When monochromatic X-rays strike the sample, polychromatic fluorescent X-rays are generated (because usually samples consist of a number of elements). Via a collimator (kind of lens) these are directed to a crystal (e.g. LiF) which has been cleaved and positioned in such a way that a set of planes with a known d-value can be used to diffract the incident waves. By turning the crystal, the angle θ of the incident beam can be varied so that diffraction can be obtained for all possible wavelengths λ which are characteristic for the elements in the sample. Recording is obtained with a detector which moves at twice the angle speed (otherwise the beam would not be caught). Thus, because here the unknown wavelengths λ are determined with a known value of d, this is the opposite procedure of X-ray diffraction analysis.

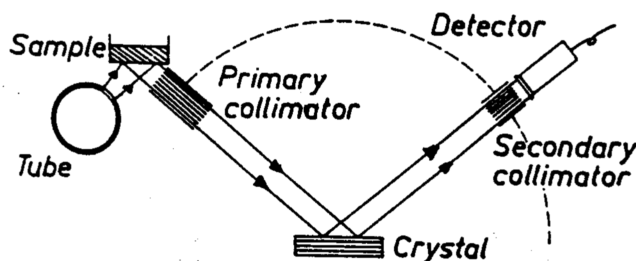

Fig. 11. The principle of X-ray fluorescence spectroscopy.

X-ray diffraction analysis of soil samples

The most usual procedures of XRD in soil analysis make use of the following samples or specimens:

1. powdered samples of the whole soil or of separated silt or sand fractions
2. oriented or, less usual, random samples of the separated clay fraction

For powdered and random clay samples both the diffractometer and the camera can be used; oriented clay specimens are almost exclusively run on the diffractometer.
There is good reason for (parallel) orientation in the clay[4] specimen. Clay minerals are all phyllosilicates with a platy structure and habit. Therefore, the spacings between the

[4] The term *clay* may give rise to confusion. *Clay minerals* are secondary silicates, almost exclusively phyllosilicates, usually occurring in the *clay fraction* which is a *size* fraction, normally the fraction < 2 μm. Thus, the clay fraction does not only contain clay minerals but also other minerals.

individual basal crystal planes (with indices *001*) are the main characteristics for identification in XRD. When the clay mineral particles are parallel oriented on the specimen holder, diffraction by the basal planes is favoured leading to stronger reflections and better identification, particularly for clay minerals present in small amounts or with imperfect crystallinity. Parallel orientation is obtained by sedimentation of the clay from suspension onto the specimen carrier, for instance by pipetting drops of a suspension on a glass slide or by drawing the suspension through a porous slide by suction. Smearing of a clay paste with a spatula onto a slide is sometimes practised also. The orientation of the clay minerals usually does not impair the reflections of the other minerals in the clay fraction (e.g. feldspars, quartz, calcite, iron oxides etc.) which, moreover, usually have sharper reflections (except the Fe-oxides).
Identification of the minerals is done by comparing the obtained peaks with the fingerprints of known minerals which can be found in various reference files. An experienced operator will only need these files in case uncommon minerals are encountered.
A number of minerals commonly found in the clay fraction of soils is given in Table 1.

Table 1. Some minerals commonly occurring in the clay fraction of soils.

Basal spacing	Clay minerals	Non-clay minerals
7Å	kaolinite halloysite	feldspars quartz calcite
10Å	illite (mica)	oxides and hydroxides of
14Å	vermiculite smectite (montmorillonite)	Fe and Al e.g., hematite, goethite, gibbsite, ferrihydrite etc.
14Å	chlorite	
	various intergrades	
"amorph."	allophane imogolite	

X-ray fluorescence analysis of soils

Basically, two types of specimens are used:

1. soil (or clay) finely ground and pressed into a tablet
2. soil (or clay) molten into a bead at high temperature (ca. 1200 °C)

The tablets or beads are scanned in the XRF spectrometer and the reflection intensities are digitized and recorded. (For qualitative monitoring, e.g. to find out the presence of a certain element, a recorder print-out with the characteristic reflections, similar to an XRD, can be produced). The digitized results are compared by computer with those of synthetic standard samples and the results are automatically produced. It is worth noting that very "light" elements i.e., below Na in the periodical system, cannot be determined with XRFS. This excludes the in soils important elements carbon and nitrogen.

Because of considerable matrix effects, for good accuracy it is important that the composition of the standard samples approaches that of the unknown sample as closely as possible. This may be achieved by circumstantial knowledge of the unknown sample or by prescanning. Matrix effects consist of both *absorption* and *enhancement* effects. Put simply, it could be said that photons of characteristic radiation excited in one element can be used to excite photons of characteristic radiation in another element. Thus, radiation of the first element is absorbed and suppressed whereas that of the second is enhanced. This is illustrated in Fig. 12. Looking from right to left it can be seen that at a wavelength of 2.07 Å

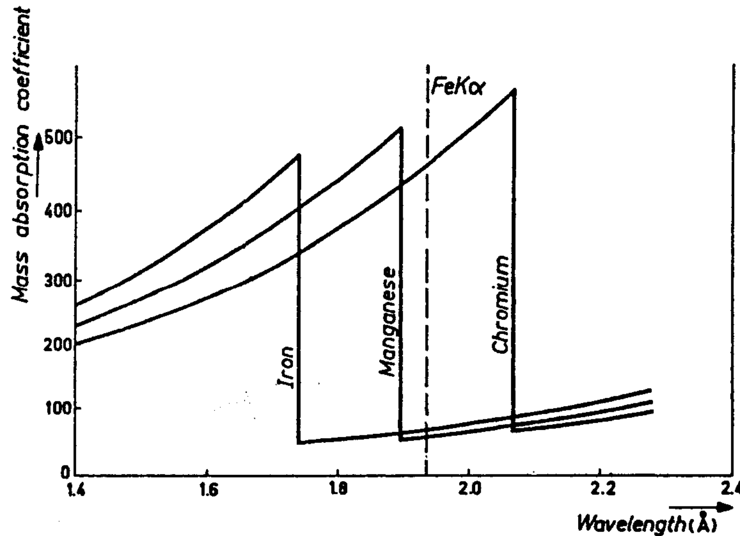

Fig. 12. Origin of absorption and enhancement effects in high alloy steels.

radiation is strongly absorbed by chromium in the sample because electrons of the K-shell are knocked out of their orbital. This called an *absorption edge*[5] in the absorption curve. Manganese and iron show such absorption edges at 1.89 and 1.73 Å respectively. Now it can be seen that if iron is measured by counting its Kα radiation (at 1.93 Å) in the presence of chromium this radiation is strongly absorbed whereas in the presence of manganese this absorption is virtually absent.

The detection limits of XRFS are particularly important for trace elements. From the foregoing it will be clear that the countable radiation is influenced by several factors of which matrix, background radiation and atomic number of the elements are the major ones. Fig. 13 gives an impression as to how the detection limit of elements varies in a certain matrix.

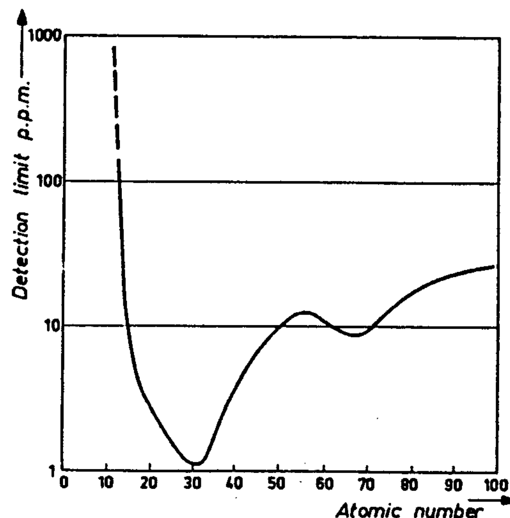

Fig. 13. Variation in detection limit with atomic number for an average matrix.

[5] An absorption edge occurs when photons have just enough energy (with corresponding wavelength) to cause characteristic radiation.

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