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A PRACTICAL METHOD FOR OPTICAL SPECTROSCOPY OF CRYSTALS

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SUMMARY

In this article a recently developed method for optical spectroscopic analysis of crystallized substances is introduced. The practical method proposed is non-destructive, and the apparatus required is relatively simple and inexpensive.

Principles of optical spectroscopy for the analysis of trace elements in complex crystals are reviewed; essential aspects of this method and other routine methods are compared.

Next, the nature, scope, and limitations of the new practical method are discussed, and the information, which can be obtained, is summed up. In essence, the procedure consists of the sequential registration of absorption- and luminescence spectra of the substance to be examined, and the subsequent analysis of both spectra.

Details of the apparatus required, and of the analysis procedure are treated in the following section; different methods for obtaining good quality absorption- and luminescence spectrograms are reviewed here. An important feature of the method is the excitation of luminescence with blue radiation; the advantages of its use are critically discussed.

Facultative refinements of apparatus and method, making possible polarisation spectrography and topographical spectrography of macrocrystals, are indicated.

Requirements for preparations for the purpose of calibration are mentioned.

The practical value of the new method is demonstrated by results, obtained in the process of determination of some definite typochemical varieties of the crystallized minerals scheelite, apatite, zircon, spinel and topaz; these varieties are described. Finally, possible applications in the fields of mineralogy, gemmology and geochemistry, chemistry and physics, and even in industry, are reviewed. It is expected, that the proposed method will develop into a practical tool for routine researches in these branches of science.

1. INTRODUCTION

Optical spectroscopy of crystals is a powerful tool for the analysis of complex solid compounds; it can be applied in the fields of chemistry and physics, and in mineralogy and geochemistry. With its aid, it is not only possible to identify trace elements in crystal lattices to determine – semi-quantatively – their concentration, but also to obtain other important data, like the valence of their ions, modes of incorporation in the host-lattice, ion group configurations, and modes of space charge-compensation.

In this article, a new method is introduced, with the aid of which trace-elements in crystallized solids can be analyzed by their absorption- and luminescence spectra. The apparatus, designed for this purpose, simple and relatively inexpensive as it is, makes it possible to obtain good quality spectrograms in a relatively short time. This proves, that optical spectroscopy is not only a tool for highly trained specialists exclusively, having varied types of sophisticated apparatus at their disposal, but that the method can be adapted to suit practical work in many fields of applied sciences by merit of its simplicity, low cost and – above all – its flexibility.

The nature of the new method is such, that no extensive training for operating personnel is required.

2. PRINCIPLES OF OPTICAL SPECTROSCOPY OF SOLIDS

2.1 In order to bring forward, in a clear way, the characteristics of solid spectroscopy, it might be helpful, before discussing details of the method, to explain differences between current spectroscopic methods and the proposed optical-spectroscopic method.

The purpose of "normal" spectrocopic methods is to determine the elements of which the substance to be analysed is composed and their concentration. To permit this, the substance, or a sample of it, usually has to be vaporized at extremely high temperatures; in the vapour, energy transitions involving optical effects, characteristic for free ions, can then be observed. In actual practice, we are taking spectrograms of the light, *emitted* by the vapour, or light, *transmitted* by the vapour: emission- and absorption-spectrograms respectively. The spectral lines registered are characteristic for the elements, present in the vapour, and their intensities are a direct measure for their concentrations. There are, in this case, very few interfering effect, which could influence emission. Some practical methods are:

- Emission spectrophotometry
- Laser-micro-emission spectroscopy
- Atomic absorption spectrophotometry

1) Grote Stegel 13 Eijgelshoven (L).

These methods can be qualified as being "destructive", because at least a part of the object must be vapourized, that is: decomposed. In the case of examination of expensive synthetic crystals, or rare natural crystals – individual objects of value – this can be a prohibitive disavantage.

Then, we would like to mention the method of X-ray fluorescence spectroscopy. In this case, it is not necessary to decompose the substance of the object completely, but it is necessary to prepare a powdered sample. Therefore, the method cannot be qualified as being non-destructive. The X-ray fluorescence analysis yields only data about the elements present (with certain restrictions) and their concentration.

Crystal spectroscopy, on the contrary, is a purely optical, in itself non-destructive method: by using appropriate radiations for the generation of spectra, no alterations are taking place during the examination of the substance. In addition, it is possible to obtain more information about a complex substance than with the preceding methods. Apart from data about elements present and their concentrations, we can obtain information about the structural composition of the object, already mentioned in the introduction. As the spectra of some trace-elements are very characteristic in different substances, it is very often possible by analysis of their optical spectra, to determine the nature of the host-lattice, if this should be unkown. To sum op, the optical spectroscopy method is non-destructive, and yields a maximum volume of information.

2.2 This information is obtained by analysis of two types of spectrum, e.g.
– the absorption spectrum, and
– the luminescence spectrum.

Here, it is necessary to elucidate the special character of optical spectra of crystals. Spectra of free ions of the elements are usually pure line-spectra; some of them are extremely complex, like the iron spectrum, which shows thousands of lines in the visible range. Spectra of ions or ion-groups in crystals are usually much simpler. In crystals, only a limited number of elements show line spectra; others show a few more or less wide bands.

Thus, spectra of complex crystals show lines and bands. This may complicate the analysis of the spectra: sometimes the bands are so wide, and of such intensity, that diagnostic lines of other elements are masked. Some groups, like WO_4^{2-}, MoO_4^{2-} or UO_2^{2+} form active centres of luminescence, and can emit wide and intense bands in important spectral regions. Other, more serious complications are present, when the crystal contains several different active ions or ion-groups. In this case, processes of energy transfer from one type of ion to another can take place, causing the intensity of luminescence of one kind of ion to increase, and that of other ions to decrease or even to quench their luminescence completely. Discussion in detail of these effects, however, is not opportune in the cadre of this article.

Another important feature is that the crystal-spectrum of one element is not only characteristic for the state of its ion, but also for the local crystal field. The spectra of neodymium, for example, are different in the oxyde Nd_2O_3, in the complex tungstate $CaWO_4 \cdot Nd^{3+}$, the complex fluorapatite $Ca_5.F.(PO_4)_3.Nd^{3+}$, or the complex fluorcarbonate, called parisite $Ca_2.Ce[F|(CO_3)_3].Nd^{3+}$. This effect is caused by the influence of the electric field in the crystal on energy states of the incorporated active ions. In some ions, the influence of this field is strong, in others it is much weaker. The influence of the crystal field is particularly small in case of ions of the lanthanides, or "rare earths". Here, energy-changes take place in the inner "N" shell, which is shielded from the external crystal field by two outer shells (the "O" and "P" shells). Therefore, the lanthanide spectra are not strongly influenced by different crystal fields: the same characteristic grouping of lines of an element is observable in the "O" and "P" shells). Therefore, the lanthanide spectra are not strongly influenced by different crystal fiells: the same characteristic grouping of lines of an element is observable in the spectrum of this element in different host lattices.

The influence is somewhat more pronounced in the case of ions of the transition elements: these possess one outer electronshell providing partial shielding. In this case, the spectra of one element in different host lattices show more important differences. A demonstrative example is the ion Cr^{3+}, showing different spectra in the lattices of corundum (ruby), spinel (red gem spinel), chrysoberyl (alexandrite) and beryl (emerald). The grouping of the chromium lines is still very similar in all these lattices, however.

2.3 From the preceding, it will be clear, that the method of anallsis of optical crystalspectroscopy has certain limitations.

Only element- host lattice *combinations*, possessing good absorption- and/or luminescence spectra can be analysed. There are elements with good absorption spectra, not showing characteristic luminescence in the wavelength range, utilized for analysis, for example Fe^{2+}, Fe^{3+}, U^{4+}, Nd^{3+} [1]. Other elements do not show good absorption spectra in the same wavelength range, but possess very intense and characteristic luminescence spectra, such as Sm^{2+} and Sm^{3+}, Dy^{3+}, W in WO_4^{2-} etc.

It will be clear, that the range of analysis is largest, when both absorption and luminescence spectra are evaluated, and when the wavelength-range for analysis is as wide as practically possible. Therefore, characteristics of the proposed instrumental method are:

– Registration of two types of spectrum, absorption- and luminescence-, one after the other in one action, with equal facility.
– Registration of spectra on photographic plates, in a wavelength range between 380 nm and 1000 nm. In this range, glass optical elements (lenses, prisms etc.) can be used instead of more expensive materials like quartz or fluorite.

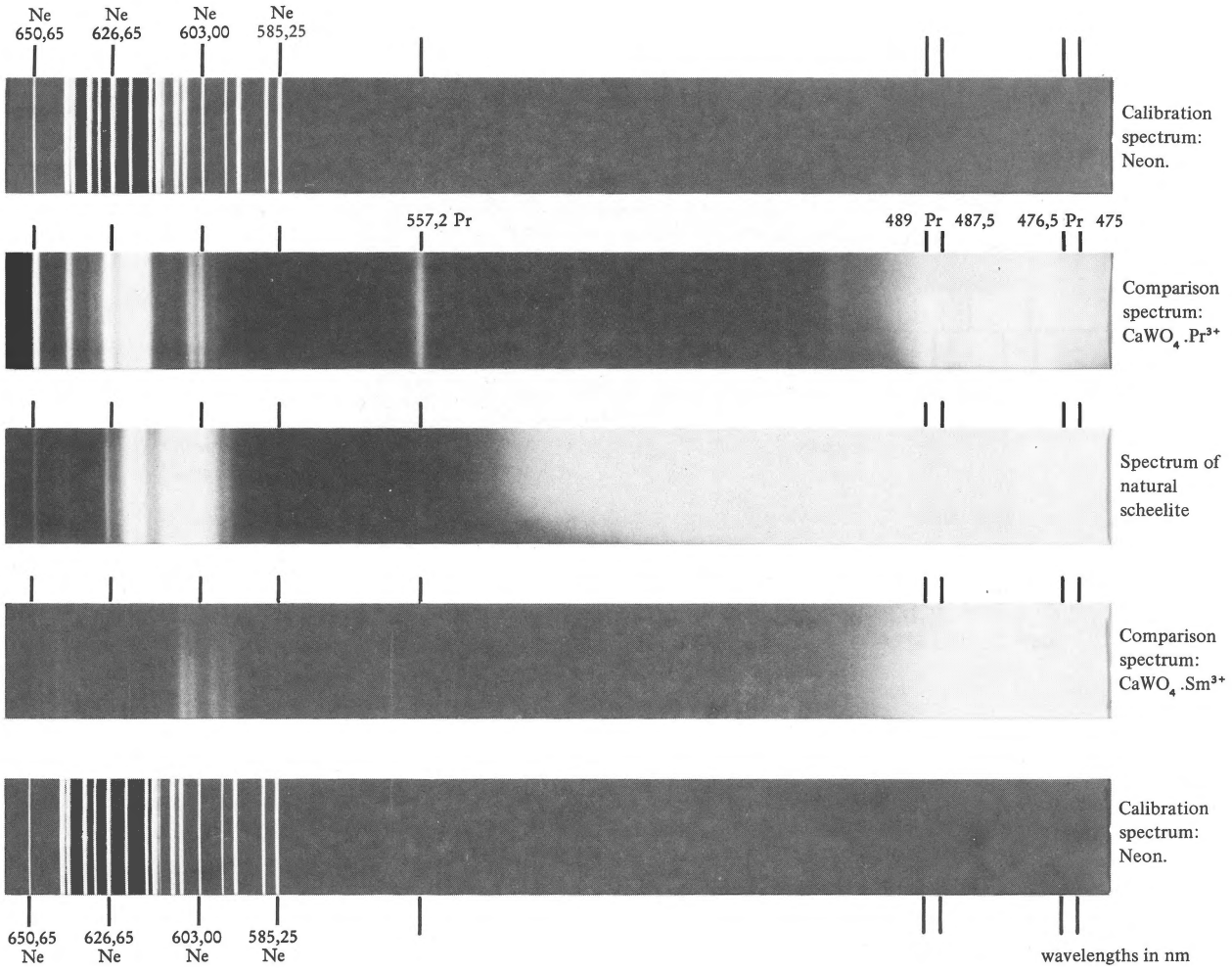


Fig.1
Luminescence-spectrum of a natural scheelite, with comparison-spectra of "standard" substances, and calibration spectra.

Photographic registration has prominent advantages, which we would like to sum up as follows:

- extremely high resolution of closely spaced spectral lines,
- high, cumulative sensitivity
- wide-range sensitivity for different wavellngths
- exact, durable, and easy to handle documentation of results
- inexpensive, light-weight equipment. Glass optical parts are quite satisfactory.

Of course, there are other factors, which tend to limit the field of application of crystal spectroscopy. They are related to the nature of the host lattice, structural degenerations and defects, the presence of attenuating ions or ion groups etc. However, the scope of this article does not permit a detailed discussion of these factors.

2.4 To conclude this section, the information, which can be obtained by crystal spectroscopy is recapitulated:

- Trace elements present, if optically active as ions in a host-lattice.
- Valence of their ions
- Concentration of ions (semi-quantatively)
- Nature of the host-lattice
- Modes of substitution of active ions in the host-lattice
- Modes of space-charge compensation in the case, where the valence of the substituting ions differs from the valence of the ions replaced: for example, trivalent lanthanide ions Ln^{3+} can replace Ca^{2+} ions in many compounds.

[1] Nd^{3+} shows very prominent luminescence lines in the infrared region.

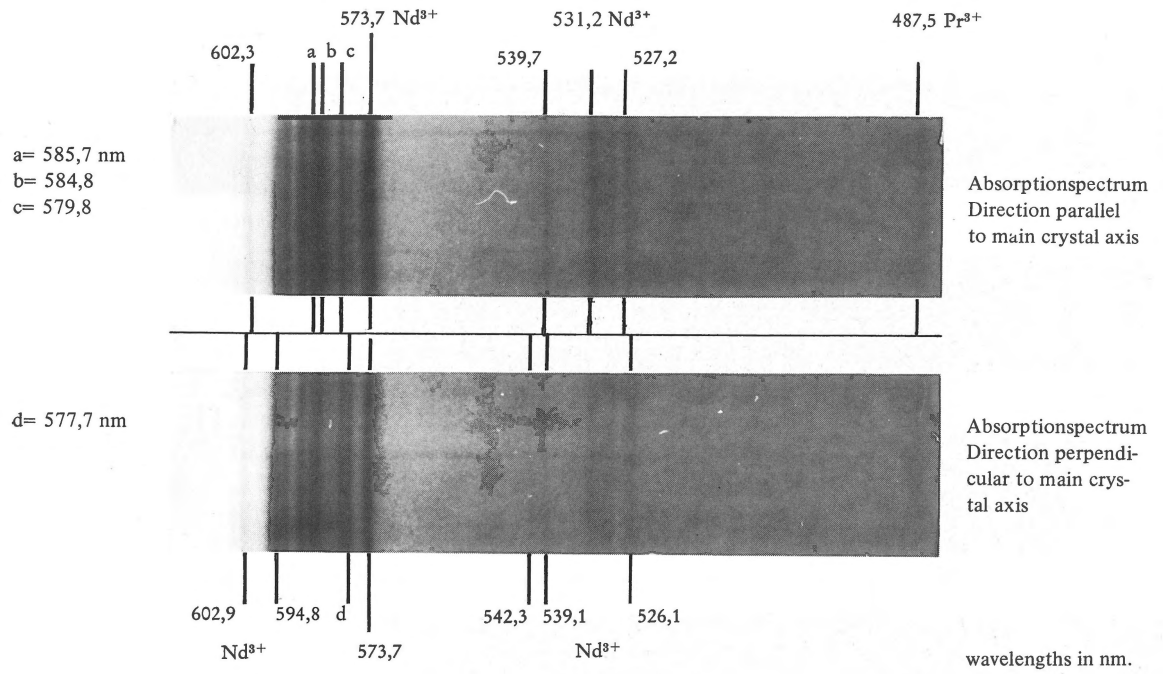


Fig. 2
Polarized absorption spectra of a natural scheelite.

3. DESCRIPTION OF A PRACTICAL ANALYSIS METHOD; DETAILS OF APPARATUS AND PROCEDURES

3.1 Before going into details, it seems useful to describe in general the method of analysis, and the apparatus developed.

In the preceding part, the importance of the taking of both absorption- and luminescence spectrograms was demonstrated. For a complete analysis, all lines and bands registered will have to be identified. This can be done in two ways:

A. By measurement of the wave lenghts of the lines; subsequent identification by comparison with known wavelengths of active ions in the lattice in question.

Here, as it is customary in emission-spectrography, spectra for wavelength calibration (usually the iron spectrum), are registered simultaneously with the spectra of the object. By measurement of the relative positions of these lines and interpolation, wavelengths can be determined accurately. If we then have a table at our disposal, listing characteristic wavelenghts of active elements in the given host-lattice, the elements present can be identified by their wavelenghts.

Apart from the fact, that we do not dispose of such tables for a satisfactory number of substances, it must be said, that this procedure is an exceedingly laborious one.

B. Direct identification of lines with the aid of comparison spectra of "standard" substances.

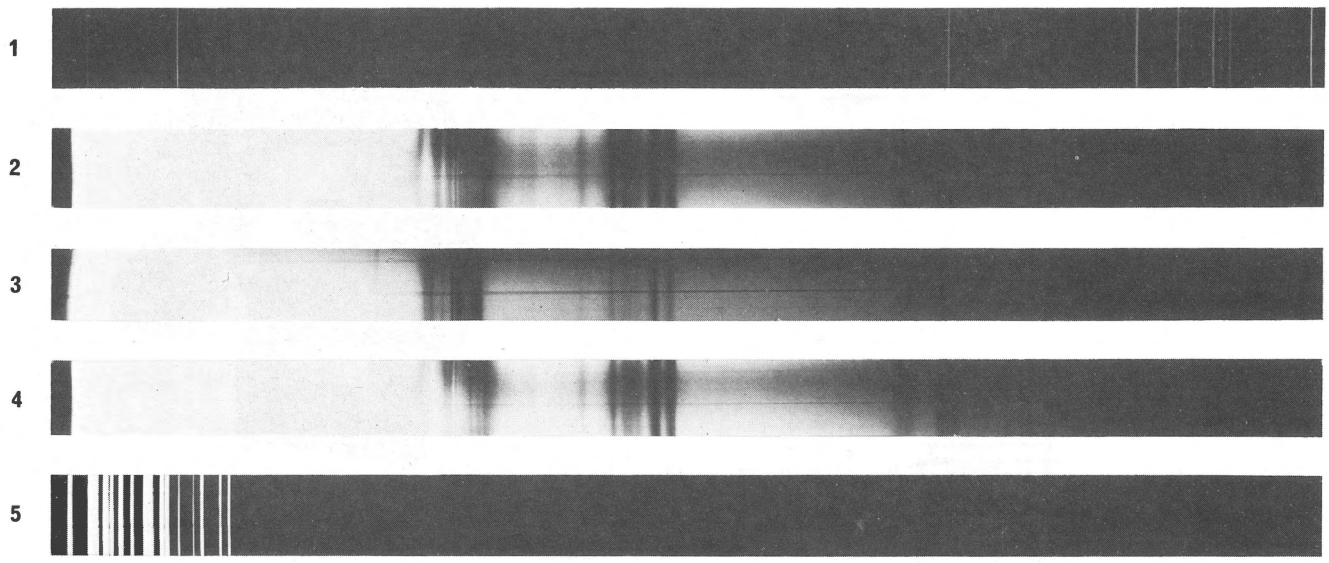
Here, it is necessary to dispose of a series of "standard" preparations, consisting of the same chemical compound as the object of analysis, and doped with a single trace-element in a known concentration (for example, one atomic percent).

We then take spectrograms of the object, with adjoining spectra of different "standard" preparations. The trace-elements can be identified by coincidence of lines.

In fig. 1 such a spectrogram is shown. The top and bottom strips are neon-spectra for wavellngth calibration purposes; the central strip is a luminescence spectrum, excited by blue radiation, of the object – a natural scheelite –; the adjoining spectra are luminescence spectra of the "standard" substances indicated. The coincidence of Pr^{3+} and Sm^{3+} lines with lines, proper of the object, is indicative of the presence of these ions in the object.

The second method, B, is much simpler and more rapid tha the first, but a complete series of "standard" preparations is required. These preparations can eventually be manufactured under standardised conditions in series.

If it is desired to make semi-quantitative analyses, it is essential to dispose of such series of "standard" preparations. In this case, the concentration of the trace-ellments can be estimated by comparison of the intensities of the lines of a



1. Calibrationspectrum of Argon
2. Absorptionspectrum of $CaWO_4 . Er^{3+}, Na^{1+}$, polarized parallel to main crystal axis.
3. Absorptionspectrum of erbiumscheelite.
4. Absorptionspectrum of $CaWO_4 Er^{3+}, Na^{1+}$, polarized perpendicular to main crystal axis
5. Calibrationspectrum of Neon

Fig. 3
Polarised absorption spectra of $CaWO_4 . Er^{3+}, Na^{1+}$, compared with the absorption spectrum of a natural Er^{3+} containing scheelite.

certain element in the object with the intensities, generated in a "standard" preparation of a known concentration. For lack of space, the pro's and con's of this method cannot be discussed here.

It is also possible to obtain information about structural details of the objects of examination by analysis of polarized spectra.

In fig. 2, an example is shown of a polarized absorption spectrum of a natural scheelite with a high neodymium and praseodymium content. Their trivalent ions replace Ca^{2+} in the tungstate.

If we dispose of synthetic macrocrystals, it is even possible to obtain data about space charge compensation modes. If we compare, for example, the absorption spectra of a crystal of $CaWO_4 . Er^{3+}, Na^{1+}$, where the excess charge of the Er^{3+} ions is compensated by the deficit of charge Na^{1+} ions in Ca^{2+} locations, with the absorption spectrum of a natural scheelite with Er^{3+} in Ca^{2+} locations, clearly observable differences show, that, in the natural scheelite, no space charge compensation by Na^{1+} can be observed. Here space-charge compensation is effected by vacant (Ca^{2+}) locations.

These spectra are shown in fig. 3. The difference between the absorption spectra of the synthetic- and the natural substance is quite striking in the left groups.

3.2 After all this rather abstract reasoning, a short explanation of the apparatus, which was developed for our analysis-method, must be given:

A general scheme is shown in fig. 4.

It shows a set-up, suitable for the registration of absorption- and luminescence spectra – these with excitation by blue or ultraviolet radiations – of crystals and opaque substances. Normally, for both types of spectrum, an incandescent lamp is used as light source. High-power (between 250 and 1000 Watts), low voltage hallgen-cycle lamps with a very small filamentary structure are to be preferred. By means of the mirror 11 and the lens 13, a parallel beam of high intensity is formed. At location 10, appropriate light-filters for the isolation of a definite range of wavelengths ("bandpass-filters") can be inserted. The filtered light is concentrated on the object 7 by lens 9. In this manner, very high energy densities can be obtained. The object is fixed in a manipulator 5 (patent applied for), with

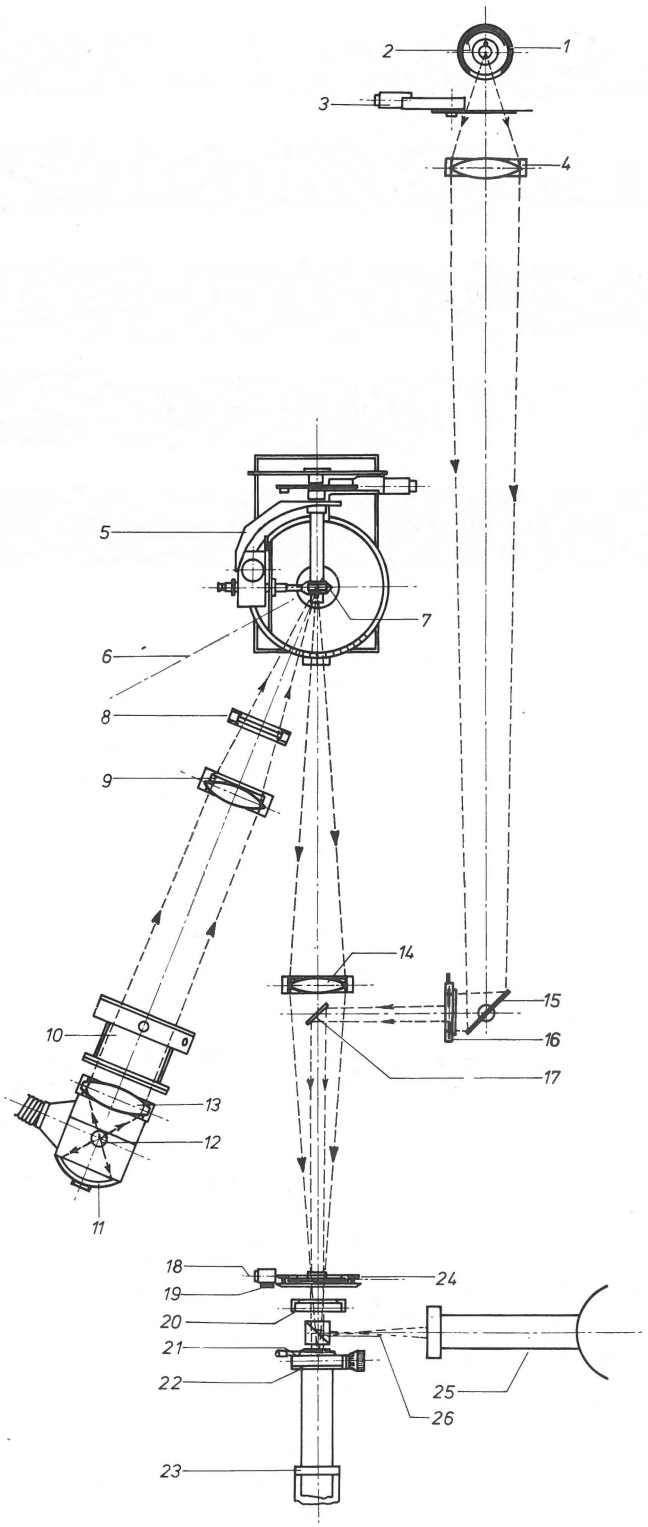


Fig. 4
Apparatus for the registration of polarized absorption- and luminescence spectra of crystals.

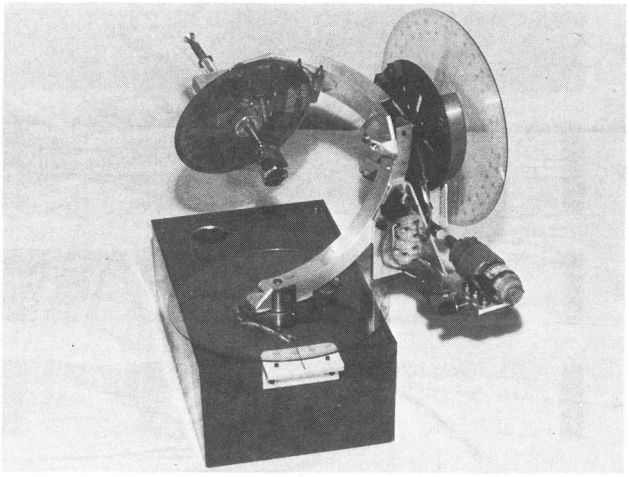


Fig. 5
Experimental model of an object-manipulator.

the aid of which it can be rotated about three mutually perpendicular axes in space; a photograph, fig. 5, shows an experimental model of this so-called "tri-axial goniostat".

The object re-emits a part of the incident radiation and emits characteristic luminescence. These radiations are concentrated by lens 14 on the slit of a spectrograph with photographic registration 23. With this instrument, the re-emmitted light (absorption spectrum) and the luminescence (luminescence spectrum) are analysed. At location 20, suitable filters for registration-wavelength range selection in absorption spectrography, or for the suppression of exciting radiations in luminescence spectrography, can be inserted in the analysis-beam. At location 18, a polarizer, which can be rotated and positioned exactly, can be placed if it is desired to register polarized spectra. For the registration of spectra for the purpose of wavelength-calibration, the light of a gaseous discharge lamp 1 is directed on to the spectrograph by means of lens 4 and the mirrors 15 and 17.

For the excitation of the object with ultraviolet light, a small size source can be located at 6; the Philips HPK 125 W is a suitable lamp.

3.3 We now are coming to the technique, necessary for obtaining absorption- and luminescence spectrograms of an optimal quality. Absorptionspectra are produced by irradiation of the object with continuous light in the wavelength-range suitable for analysis; in our case this range lies between 380 and 1000 nm. Usually, this light has to pass through the absorbing medium; an example is the spectral absorption analysis of chemical compounds in solutions. If this method is to succeed with crystals, the following conditions must be fulfilled:

- The object, a crystal, must be sufficiently transparent to permit registration of non-absorbed radiation.
- The absorption path must be of sufficient length.

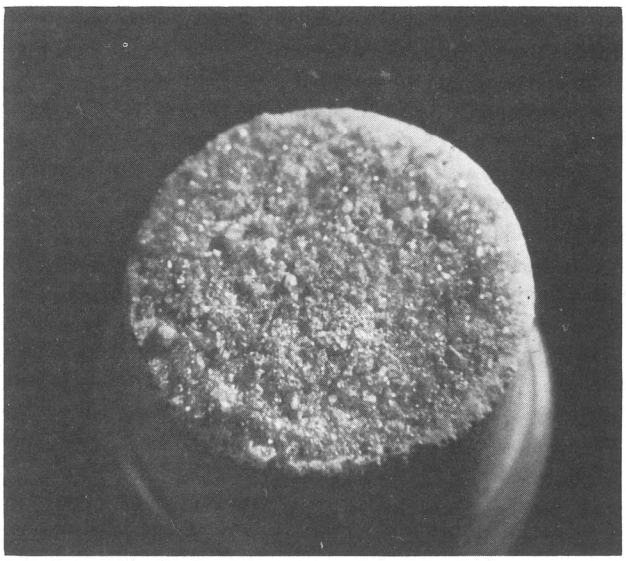


Fig. 6
Object, prepared for the examination of a crystal powder. Photomicrograph; magnification 2,5 x

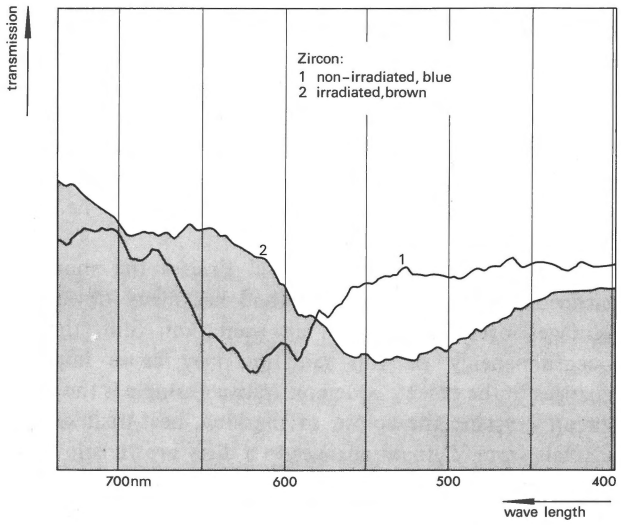


Fig. 7
Superimposed spectrophotograms of non-irradiated and irradiated zircon from Vietnam.

Frequently, for the purpose, planparallel plates will have to be cut from crystals which are translucent or opaque. But this we regard as a destructive procedure.

Very often, crystals at our disposal are of small size. Concentrates from ground minerals are a good example.

With the new apparatus proposed, it is possible to generate good absorption spectra; here the light *re-emitted* by the object is analysed. In the case of crystal powders, we have applied these in a layer of sufficient thickness on a ceramic base. This preparation is then mounted in location 7 in fig. 4. By using incident light of sufficient intensity, striking the object at an appropriate angle of attack, excellent absorption spectra can be obtained. This method works also in the case of an opaque crystal. Fig. 6 shows an example of a crystal-powder object.

A very important factor in increasing the sensitivity of analysis by luminescence is the method of excitation. Ideally, the method selected should be equally effective for all trace-elements to be analysed; it should be as simple and inexpensive as possible, and the radiation used should not cause changes in the object.

In the first place, we will discuss – shortly – the problem of non-selectivity of the exciting radiation. It is possible to determine, for any substance containing active trace-elements, an optimal method of excitation. This can be demonstrated by some examples:

- Ruby, red spinel, chrome-diopside, sodalite, strontianite. Here, long wave ultraviolet radiation (Hg 365 nm) is most effective.
- Apatite, calcite, scheelite. Short wave radiation of a wavelength below 300 nm, for instance Hg 254 nm, is optimal according to current sources of information. It is certainly extremely effective for the excitation of visible luminescence.
- Zircon. Cathode-ray excitation is of maximum effectiveness, but it is highly selective for certain elements.
- Cassiterite. Luminescence can best be excited with hard X-rays.
- Spodumene. Here, cathode-rays and gamma-rays are the most effective means of excitation.

Systematically, the following means of excitation can be distinguished:

Electromagnetic radiation	*Corpuscular radiation*
– Light in the visible range	– Cathode-rays
– Long-wave ultraviolet radiation	– β-rays
– Short-wave ultraviolet radiation	– ion-rays (low energy)
– X-rays	– α-rays or high energy ions
– γ-rays	– neutron beams

From this list, it will be clear, that many otherwise effective methods are entirely impracticable for routine analysis. Other methods have serious disadvantages, and their usefulness is limited. As an example we will take the case of excitation with cathode-rays:

The apparatus required here is expensive; it involves a regulated high voltage supply system, and vacuum pumping equipment. The object must be placed in high vacuum (10^{-5} mm mercury or less), and is subjected to electron (and some ion-) bombardment, causing intense local heating. All these

effects can cause serious destructions in the object, such as: de-hydratation, lattice degradation, introduction of foreign ions etc. Then, some crystals contain occluded gases or volatile matter; this makes it sometimes impossible to attain the desired vacuum. In addition, this G^{as} causes emission of undesirable spectral lines. In short: the method is complicated and expensive, and irreversible changes can be caused in the object.

Next to cathode-rays we will discuss the short-wave ultraviolet radiations. This method has many obvious advantages over the cathode-ray excitation. Still, the high quantum-energy of this radiation may cause important changes in the object. A demonstrative example is the case of zircon crystals: the colour of the blue, heat-treated zircon crystals from Vietnam changes to a dirty brown colour after only ten seconds of irradiation. This change in colour indicates a change of valence of the colouring ions. The importance of this change is demonstrated by the superimposed photometric diagrams, shown in fig. 7. The chemical activity of this radiation is thus proved to be deleterious to accurate analysis.

Many sources of this radiation, gas-discharge tubes, contain noble gases (helium, neon and argon), which emit strong lines in the infrared region, important for analysis. The commercially produced blocking-filters, such as "Wood's" glass, are transparent in this region, and the interfering lines appear on the spectrogram. They can seriously impair the detection of trace-element lines.

3.4 To avoid the disadvantages, mentioned in the preceding part, a new effective system for excitation of luminescence was developed. Here, use is made of blue radiation, emitted by the same incandescent lamp, that is used for the registration of absorption spectra, as explained in section 3.2. One integrated instrument can be used for absorption- and luminescence spectrography.

In the course of the authors experiments, it was surprisingly discovered, that blue radiation in the wavelength-range between 400 nm and 550 nm is very effective for the excitation of luminescence of trace-elements, including most of the lanthanides, many transition-metals and heavy metals. The discovery was made, when a scheelite – a mineral, that is allegedly only luminescent in short-wave ultraviolet light –, irradiated with blue radiation, was found to exhibit an intense orange-red luminescence. The same effect was then observed with a special variety of fluorapatite. Extensive research and testing of this system of excitation revealed its rather general effectiveness, and its lack of selectivity for certain active ions. Cathode rays are extremely selective for the excitation of Eu^{3+} and Dy^{3+} ions; short-wave ultraviolet radiations are very sellctive for the excitation of active ion groups like WO_4^{2-}, MoO_4^{2-} or UO_2^{2+} in some compounds.

The non-selectivity of the blue radiation is a great advantage if semi-quantative analyses are to be made.

The intensity of the luminescence, caused by blue irradiation, is considerable. Effective excitation of such ions as Ho^{3+} and Er^{3+} is possible in cases, where ultraviolet radiation is ineffective. With the incandescent lamp and filter system, very high densities of excitation energy can be achieved. This is very difficult with short-wave ultraviolet light.

By making a suitable choice of filters, it is easy to adapt the characteristics of the exciting radiation to the properties of a particular object.

The quantum-energy of the blue radiation is low, and no photochemical changes can take place in the object. The object is not heated to any considerable degree during excitation, especially if a cell, filled with a saturated solution of copper sulphate is placed in location 10 of fig. 4. In this pre-filter, the heat radiation from the light source is effectivell absorbed and dissipated with the aid of a cooling jacket.

Another important advantage of the blue radiation is, that it does not excite wide-band luminescence of some ions or ion-groups. Thus, the blue luminescence of WO_4^{2-} is not excited in scheelite, and in some apatites, containing Mn^{2+}, the caracteristic yellow-green band is not excited. This means, that the line-emissions of lanthanide elements can be observed without interference: they are no longer masked by the wide and intense luminescence bands.

This simple and inexpensive filtered light source has many advantages over a combination of a xenonlamp and a monochromator; in particullr, energy-losses are much smaller. This expresses itself in the exposure-time, necessary to obtain good quality luminescence spectrograms: in our case, even when a spectrograph with a dispersion of 25 Å per mm at 600 nm was employed, an exposure time of several minutes will suffice as a rule.

3.5 After having defined details of the instrumental method, we can now specify the elements, which can be analysed:

- The *lanthanides* Pr. Nd, Sm, Eu, Tb, Dy, Ho, Er and Tm in crystals of, for example: calcite, apatite, scheelite, zircon, fluorite etc. The separate quantitative analysis of these elements, with most current methods, is very difficult, especially if concentrations are small.
- *Chromium* as ions Cr^{3+} in many crystals, like corundum (ruby), red spinel, chrysoberyl (alexandrite), beryl (emerald), uvarovite, topaz, diopside, kyanite and others.
- *Manganese* as ions Mn^{2+} in fluorite.
- *Uranium* as U^{4+} or the uranyl-group UO_2^{2+} in many complex minerals and chemical compounds.
- *Platinum* in complex compounds
- *Bismuth* in calciumsulphate

Etc.

As these elements can be analysed in many different crystals, the field of application for the proposed method appears to be large enough!

3.6 The basic arrangement shown in fig. 4 permits the use of special devices, with the aid of which more detailed observations can be made. The study of polarized spectra

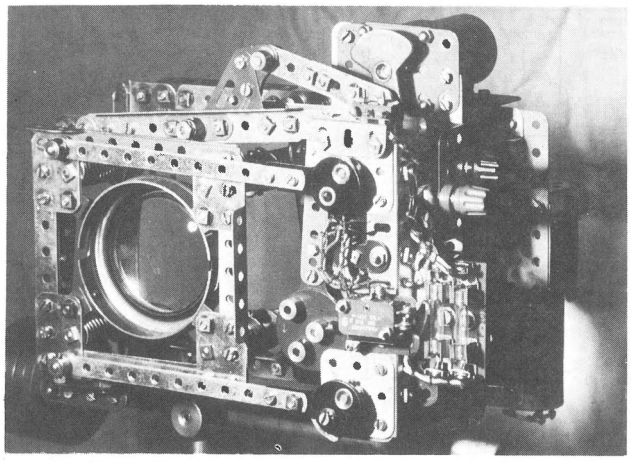


Fig. 8
Research-model of scanning lens with two-dimensional position control.

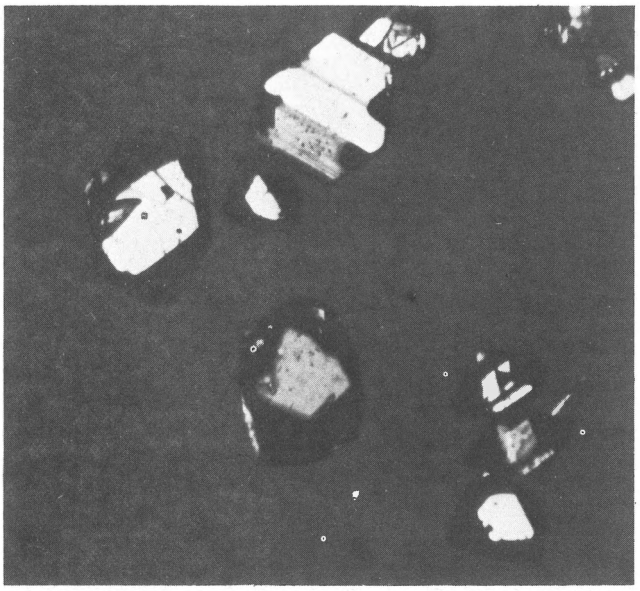


Fig. 9
Crystals of synthetical praseodymium-scheelite. Photomicrograph; magnification 130 x.

yields essential data about particularities of the crystal structure of the object. In many "doped" crystals, spectral polarization phenomena are prominent. As an example we are mentioning zircon crystals, containing Dy^{3+} and U^{4+} ions. The intense and wide yellow-green band of U^{4+} is strongly polarized perpendicular to the c-axis of the crystal, and the narrow luminescence lines of dysprosium in the "yellow" and "blue" ranges of the spectrum are alternatively polarized in directions, parallel and perpendicular to the main axis of the crystal. These effects can be observed by means of a rotating polarizer, part 18 in Fig. 4, which is provided with a graduated circle 24, and the auxiliary spectrometer 25, essential for exact adjustments. During rotation of the polarizer, spectacular changes in intensity of different spectral lines and bands can be observed. For the registration of these effects it is essential to orient the crystal-object (it may be an irregular fragment of a single crystal!) in relation to the optical axis of the spectrograph. This can be effected with the manipulator 5.

It is also possible to study the topographical distribution of elements in a larger size crystal by taking spectrograms of different regions of the object. The distribution of trace-elements in many natural crystals is not homogeneous, and in synthetic crystals it is often required to check the distribution of doping-elements. The taking of such spectrograms can be facilitated by the apparatus shown in fig. 8 (Patent applied for).

In essence, this is a special mounting for the lens 14 of fig. 4, projecting an image of the object in the plane of the spectrograph slit; this slit is shortened for this type of work. The lens is mounted in such a way, that it can execute a scanning movement in a horizontal and in a vertical direction. By remote control, the image of any desired part of the exposed side of the crystal can be projected on the shortened slit 22. It is also possible to make the lens execute an automatic scanning movement during the registration of a spectrogram. Under these conditions, we will obtain a spectrogram, which is representative for the averge composition of the exposed side of the crystal.

3.7 To conclude this section, a few remarks on the composition of "standard" preparations would be in place. In order to get correct results in analysis, one has to dispose of "standard" preparations (vide 3.1. B). The fabrication of these preparations is difficult, because the substances must be pure, and the concentration of the trace element must be known exactly. Several procedures for the composition of really good "standard" preparations were developed by the author. Fig. 9 shows a photomicrograph of a synthetic praseodymium-scheelite with a concentration of one atomic percent of Pr^{3+}.

Fig. 10 shows a photomicrograph of synthetic praseodymium-fluorapatite crystals, with the same concentration of Pr^{3+}.

Summing up, the author hopes to have been successful in demonstrating the possibility of determination, with the aid of the proposed method:

- which optically active trace elements are present in the object.
- semi-quantatively: the concentration of the elements identified.
- the type of host-lattice.
- relevant details of the crystal-structure (modes of substitution, space change compensation etc.), if desired.

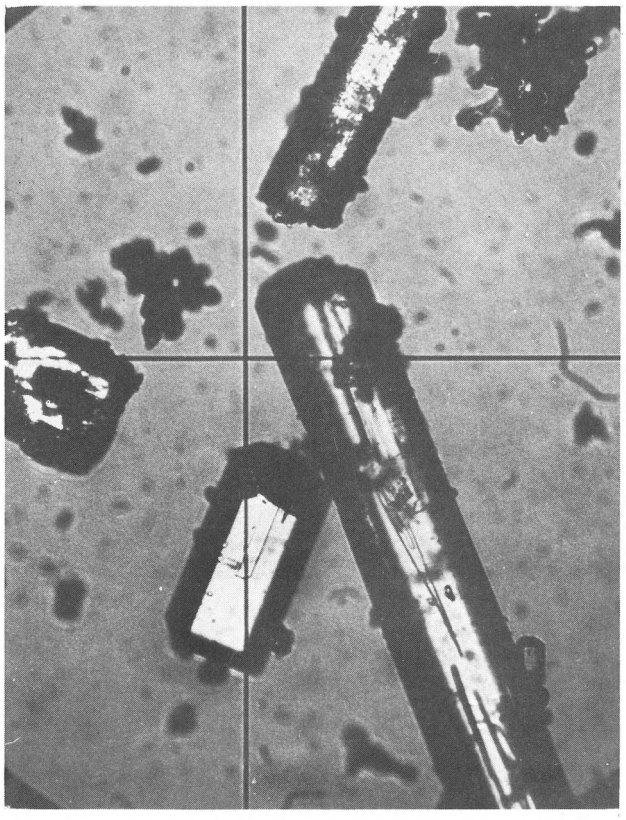


Fig. 10
Crystals of synthetical praseodymium-fluorapatite. Photomicrograph; magnification 100 x.

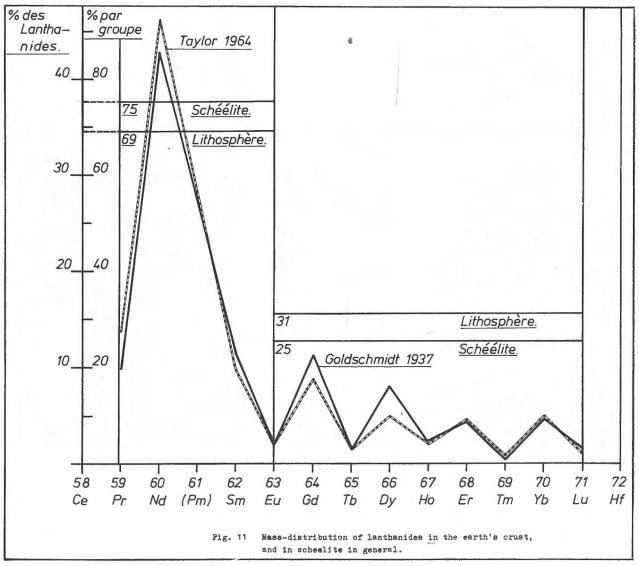


Fig. 11 Mass-distribution of lanthanides in the earth's crust, and in scheelite in general.

Fig. 11
Mass-distribution of lanthanides in the earth's crust, and in scheelites in general.

4. PRACTICAL RESULTS, ACHIEVED WITH THE PROPOSED METHOD

4.1 We will now try to demonstrate the practical value of the method by discussion of some results, obtained in the field of analysis of trace-elements in natural crystals: complex minerals. Without going into detail, we mention the fact, that several varieties of one mineral can be defined by their quantitative distribution of trace elements. These varieties are often characteristic for specific types of mineral deposits: they are called *"typochemical varieties"*. With the help of the new method, the author has been able to distinguish a number of varieties of some important minerals. A short review of these is geven below:

4.2 *Definition of typochemical varieties of scheelite*

Since the last half of last century, it is well known, that crystals of natural calciumtungstate – scheelite – often contain rare earths, or lanthanides. It is thought, that the quantitative distribution of the elements of this group shows different patterns, which are characteristic for certain varieties of the mineral. With the new method, permitting rapid analysis of lanthanide distribution, the author has examined a considerable number of scheelites from different types of deposits, and determined, semi-quantitatively, the mass-distribution of the lanthanides in them.

The lanthanides are so-called "dispersed" elements: the bulk of their total mass is distributed in all rocks, forming the earth's crust. Research-workers have succeeded in determining the *average* concentration, in parts per million, of each lanthanide ellment in all rocks, forming the earth's crust. A typical distributionpattern results, which is represented in fig. 11.

In the graph, the percentage of mass on the sum of all lanthanides (atomic numbers from 59, Pr. to 71, Lu) is given as a function of the atomic number, acoording to V.M. Goldschmidt and W. Taylor, respectively. The typical undulating distribution, showing the predominance of elements with an even atomic number over the elements with an uneven atomic number is evident. (distribution-law of Oddo-Harkins). It is also clear, that the light lanthanides are far more abundant than the heavy lanthanides: there is a *monotonously falling concentration with increasing atomic number* in each group. If we now divide the lanthanides in a group of light elements (chemically more basic than the heavy elements), including the elements Pr, Nd, Sm and Eu), and the heavier elements (Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), it will be seen, that the light elements form 69 wt.% of the total of the lanthanides, as defined here, on the average in the rocks of the earth's crust. The heavy lanthanides form only 31 wt.%.

In the same way, the distribution of lanthanides, determined by the author in 28 different scheelite crystals of differing origin, is indicated in fig. 11: the light lanthanides

form 75 wt.% of the total mass, and the heavy lanthanides 25 wt.%. In conclusion, it can be stated, that scheelite as mineral, in general shows a quantative distribution of lanthanides, which is very similar to the "normal" distribution, but with a slight preference for the light lanthanides.

Analysing the results, obtained with individual scheelites, the author made a preliminary classification, in three main types, as follows:

– *Type 0.* This scheelite-variety has a characteristic low content of lanthanides: their detection by optical spectroscopy is uncertain, which means, that the concentration of individual lanthanides is of the order of 10^{-6} or less. It is, in consequence, not feasible to determine the lanthanide distribution with certainty.

– *Type I.* This scheelite variety is characterized by a high lanthanide content and a falling quantitative distribution with increasing atomic number. The light lanthanides are present in relatively important concentrations, while the concentration of the heavy lanthanides is extremely small.

– *Type II.* This variety is characterized by a rising quantitative distribution with increasing atomic number. This rare variety was discovered by accident: a scheelite from Japan was found to show a very pronounced absorption spectrum, which the lines of holmium and erbium were prominent. Analysis revealed the quasi absence of the light elements Pr, Nd and Sm, which are far more abundant in nature. In fig. 11, the difference between the absorption spectra of a neodymium-scheelite, and the holmium-erbium-scheelite of Japanese origin is clearly visible.

The newly discovered variety was provisionally named "erbio-scheelite".

Of course, it may be assumed, that other varieties will be defined eventually, These will probably show a distribution with a maximum at a certain atomic number. Such a distribution with rising and falling distribution could be designated as Type III-66, for example, indicating a type with a dysprosium maximum.

4.3 *Definition of typochemical varieties of fluor-apatite*

Like scheelite, crystals of fluor-apatite may contain specific assemblies of lanthanides. Analyses were made of a series of fluorapatite crystals of different origin. As in the case of scheelite, it was possible to distinguish between several varieties, characterized by a typical quantitative distribution of lanthanides. It is interesting to observe, that there seems to be some sort of relation between the composition (constitutional type) and the habitus of the crystals. As the study is not yet completed, it is too early to make a definite statement about the nature of this relation.

Four typochemical varieties were defined, provisionally:

– *Type 0.* These fluor-apatites are characterized by a subspectroscopic content of lanthanides; a prominent yellow-green luminescence band is characteristic; it is caused by manganese. To this variety pertain the colourless or light-violet coloured "alpine" fluorapatites, and the greenish or red-purple coloured apatite crystals from the tin-tungsten paragenesis. The habitus is usually short prismatic.

– *Type I.* These fluor-apatites have a high content of light lanthanide elements, and a "normal" (falling) quantitative distribution. The crystals are usually long prismatic, with pyramide-faces I and II. They possess a characteristic yellowish colour, which variety hence received the name of "asparagus- stone" or "aspergolite". It occurs in iron-ore deposits of magmatic origin, or in volcanic rocks. Important deposits occur in Iran, Mexico, Spain and in the Austrian Alps.

– *Type III.* Fluor-apatites with a lanthanide distribution, showing a maximum (rising and falling distribution). In this special case the maximum occurs at the rare element europium, with the odd atomatic number of 63 (type III-63). This entirely new variety was discovered in the course of the authors researches.The well developed crystals are of a peculiar light pink colour, and display a tabular habitus, with small pyramidal faces, and vicinal faces.

The crystals are strongly luminescent in the red and blue spectral regions. The neodymium content is low in comparison to the europium and samarium contents. Typical deposits are to be found in California (U.S.A.); in the Hunsrück mountains in Germany, in the Lukmanier region in Switzerland, and at Morro Velho in Brazil.

– *Type IV.* Fluor apatites, containing uranium. This variety was also recently discovered. It occurs as coarsely cristallized masses of a greenish colour. A characteristic deposit is located in Cumberland, England.

4.4 *Definition of typochemical varieties of zircon*

Spectroscopic analyses of a large number of crystals of zircon from different deposits were made, The study is not yet completed, and some problems as yet remain unsolved. Apparently, there are three main varieties, which can be defined as follows:

– A. Zircons with a very low lanthanide content, and a very low degree of radioactivity. The colour is usually reddish brown ("hyacinth"). The crystals have no marked absorption spectrum.

– B. Zircons with a pronounced lanthanide content, and a quantitative distribution, showing a maximum (Type III, 64 or 66). Radioactivity is low (contact-photographical detection is not feasible). These zircons show a pronounced line-absorption spectrum. Characteristic deposits are to be found in Birma and Vietnam.

– C. Zircons with a uranium and thorium content. Lanthanides are also present, but in a lower concentration than in variety B. The crystals are partially metamict; the lines of the absorption spectrum are diffuse. Typical deposits are

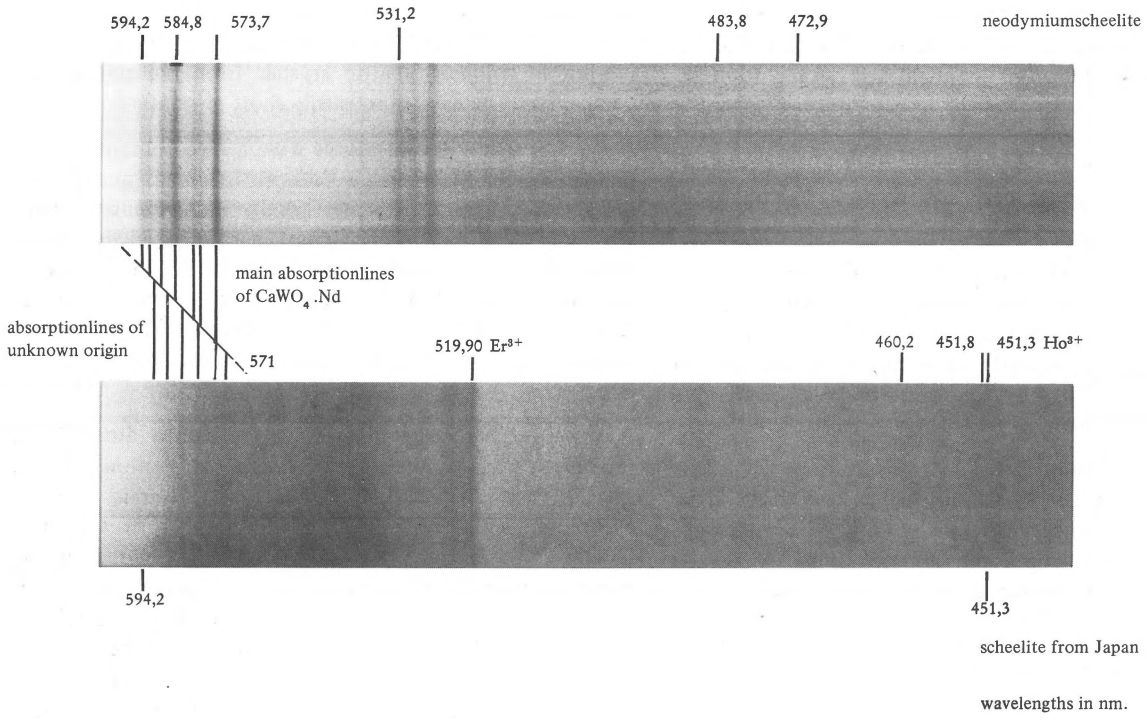


Fig. 12
Absorption spectra of neodymium-scheelite and holmium-erbium-scheelite from Japan.

located in Canada, Madagascar, and in the Miass region of the Urals.

4.5 *Structural varieties of red spinel*

The Cr^{3+} ions, colouring the magnesium-aluminiumspinels red, can serve as tracer-ions to reveal structural modifications. Extensive spectroscopic studies were made of spinel crystals from Ratnapura on Ceylon, and Kangayam, Madras, India. Two types could be distinguished, possessing line spectra with spectacularly different intensity-distributions of the chromium-lines. This is apparently an indication of the existence of two structurally different varieties, characterized by different molar ratios of MgO and Al_2O_3. Spinels with an excess of Al_2O_3, called "magnalumoxide" are also found in Yakutia, in the basin of the river Aldan.

4.6 *Varieties of topaz*

A study was made of the orange-yellow topaz crystals from Ouro Preto in Brazil. These crystals contain chromium in a dispersed phase. After heat treatment, the colour is changed to an intense pink. These heat-treated crystals show a characteristic line spectrum of Cr^{3+}; the lines are polarized. Analysis of energy levels may reveal particularities of the crystal structure, and the mode of incorporation of the chromium ions.

5. APPLICATIONS OF OPTICAL SPECTROSCOPY OF CRYSTALS

5.1 *Applications in mineralogy and geochemistry*

We will make a distinction between the identification of minerals, and the identification of typochemical varieties of minerals.

5.1.1 Rapid identification of minerals can be achieved with our method if the mineral contains optically active trace-elements, present as permanent components. In this case, the mineral can usually be recognized immediately by details of its spectra. Examples of minerals with characteristic lanthanides are:

tysonite	xenotime	
bastnaesite	rhabdophane	
parisite	wöhlerite	
monazite	thortveitite	
allanite	thalenite	etc.

Examples of minerals with a characteristic content of chromium are:

red spinel	kyanite
alexandrite	topaz
ruby	demantoid

chrome-diopside	uvarovite	
euclase	emerald	etc.

Then, all uranium minerals, containing UO_2 groups can be identified.

Finally, minerals, containing the Mn^{2+} ion, such as spessartine, triphylite, rhodochrosite and rhodonite can be rather easily identified, as well as Fe^{2+} ions in such minerals as almandine, peridot, blue spinel, cordierite, and Fe^{3+} ions in sapphire, chrysoberyl, beryl, epidote etc.

5.1.2 Identification of typochemical varieties of minerals. This problem has already been discussed. Examples are:

fluorite	pyrope garnet
calcite	zircon
scheelite	sphene
apatite	idocrase
andalusite	danburite

5.2 *Applications in gemmology*

5.2.1 The subjects of gemmological studies, valuable stones or crystals, are invariably unique.

The objects of gemmological studies can tentatively be divided in two classes:

1. The evaluation of the nature and value of precious stones; the provision of documents, in which the characteristic properties of the stones examined are stated in a strict manner.
2. Scientific research of the physical properties of rare gems. Rather regularly, discoveries of great interest for the development of solid state chemistry and physics are made here. Some examples are taaffeite, painite, ekanite, the "zoisite" from Mt. Meru etc.

5.2.2 In the course of the studies, on which this article is based, many gems have been examined by means of the new method. In this manner, it was possible to establish the practical value of this method for gemmological studies. Some advantages of the method, which are of particular importance in this field are:

- The method is essentially nondestructive. Not the slightest danger exists of damaging the gems by mechanical- or radiationeffects. Fading or alteration of colour – such an important property of gems – is excluded.
- The method is rapid; in many cases direct results are obtained. Synthetic stones, composite stones and imitations will reveal their true nature immediately.
- The spectrograms form a durable and objective document of the gem examined. It is a more effective proof of its nature than any description; a spectrogram cannot be falsified. If a large stone would be cleft and recut, it would in many cases be feasible to identify the fragments with the original by particularities of the spectra (diamond-trade!).
- It is possible to analyse stones with dimensions as small as 1 or 1,5 mm. There is no strict upper limit to the size: crystals of 60 mm can easily be analysed.
- The method and apparatus can be used in both practical gemmology and in gemmological research: accessories, which make possible polarospectrography and topographical spectrography, can be incorporated without difficulty. It is then possible to trace subtle structural details, optically active inclusions (for example parisite in Muzo-emeralds, zircon in spinel, and in almandine and spessartine garnets, xenotime in zircon, phenakite in synthetic emeralds etc.) and their orientation, for instance.

Even if the modern gemmologist disposes of various instruments and methods for the nondestructive testing of gems, it may well be, that our method will develop into an indispensable aid in this field. The apparatus required is not too expensive or complicated, and it can easily be adapted to any sort of object or experiment. The possibility of subsequent registration of both absorption- and luminescencespectra is a significant advantage in gemmological analysis.

5.2.3 To illustrate these statements, we would like to mention the following examples of gemmological operations, which were succesfully carried out with the method under discussion:

- Rapid sorting out of different gems – all of a red colour – from the Ratnapura gem gravel. It was possible to distinguish ruby, two varieties of red spinel, hyacinth (zircon), spessartine and almandine. See also section 4.5.
- Evaluation of stones, sold as "alexandrites". Among these were found: natural corundum (with Cr^{3+}), synthetic (vanadium containing-) corundum, synthetic coloured spinels, violet tinged almandine and composite stones. Some identifications could be carried out in a few minutes only.
- Distinguishing blue gem spinel.
- Sorting of different garnets.

Other examples were already treated in the sections 4.4 (zircon), and 4.6 (topaz).

It is highly probable, that the spectrographic method would be effective for distinguishing varieties of gem diamonds, as a large proportion of these show characteristic absorption and luminescence spectra with well resolved lines. Here also, absorption and luminescence spectrograms could be used for the purpose of identification.

5.2.4 In the interest of practising gemmologists, a list will be given of minerals, which are used as gems and can be analysed by means of our spectrographic methid. Species, showing good absorptionspectra are marked with A; species, showing luminescence spectra of analytical value are marked with L. If the properties A or L are generally present, this is

indicated by (G); if the properties are present only in stones from a certain provenance, this is marked by (S).

– diamond	A, L	(S)	– zircon	A, L	(S)
– spinel			– sphene	A	(S)
red	A, L	(G)	– axinite	A	(G)
other colours	A	(G)	– idocrase	A	(G)
– chrysoberyl	A	(G)	– rhodonite	A	(G)
– alexandrite	A, L	(G)	– tourmaline	A	(S)
– sapphire	A	(G)	– beryl	A	(S)
– ruby	A, L	(G)	– emerald	A(G), L	(S)
– rhodochrosite	A	(G)	– aquamarine	A	(S)
– sinhalite	A	(G)	– cordierite	A	(G)
– apatite	A, L	(S)	– diopside	A(G), L	(S)
– peridot	A	(G)	– hiddenite	A	(S)
– andalusite	A	(S)	– enstatite	A	(G)
– kyanite	A, L	(S)	– euclase	A	(S)
– topaz	A, L	(S)	– sodalite	A(S), L	(G)
– andradite	A	(S)	– lapis-lazuli	L	(S)
– pyrope	A	(G)	– orthoclase	A(S), L	(S)
– almandine	A	(G)	– danburite	A(S), L	(S)
– spessartine	A	(G)	– scapolite	A(S), L	(S)
– uvarovite	A	(G)			
– epidote	A	(G)			

5.3 *Applications in chemistry and physics*

In these fields, the analytical method can be used for:
- study of details of crystal structures
- study and development of new types of crystals for important technical applications, like quantum-generators, non-linear optics. Here, it is recommended to study intensively crystal-types occurring in nature: their examination, might reveal the existence of still unknown structures. Mineral crystals are sometimes formed under circumstances, which are difficult to reproduce even in modern laboratories.
- Quality-control during the growing process of synthetic crystals. Our non-destructive method allows the checking of homogeneity and activator content.
- Development of new luminous substances.

5.4 *Applications in industry*

The non-destructive spectroscopy-method can be used for:
- Quality-control during the series-production of crystals: it can be applied for product-control as well as for process-control. Important parameters are: the distribution pattern of "doping" elements in the crystals, homogeneity of crystal structure, the concentration of "doping" elements; the presence of separated solid phases and their orientation, etc.
- Process-control in the production of luminous substances. It is stressed once again, that the non-destructive character of the proposed method is a unique advantage; in addition, no irreversible changes are caused in the objects or products examined. These objects may be unique natural or synthetic crystals.

6 LITERATURE

It is difficult, in the case of an article of this kind, to give literature references, which are of a sufficiently general nature. Another reason is, that the method proposed – as a practical method – is new. We would like to advise interested readers to read the authors dissertation (State University of Utrecht), entitled "Une nouvelle méthode polarospectrographique, appliquée aux recherches typochimiques des minéraux". An ample list of special literature is given in this book.