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THE FLUORIMETRIC DETERMINATION OF URANIUM IN MINERALS AND WATER WITH SPECIAL EMPHASIS ON LASER-FLUORIMETRY

Abstract. Conventional uranium fluorimetry is reviewed in brief. The role of interfering substances ("quenchers") is elucidated and methods are outlined, how these difficulties can be overcome. The new concept of the "quenching function" is discussed in detail, advantages and disadvantages of classical uranium fluorimetry as well as some analytical results are shown. The improved fluorimetric determination of uranium in minerals using a laser instrument is explained in principle, some practical methods and developments are presented.

INTRODUCTION

In the present days, when uranium has become of outstanding importance as the source of nuclear energy, the analytical chemistry of this element and especially its trace analysis have developed rapidly. New techniques have been introduced such as neutron activation, delayed neutron, fission track and X-ray fluorescence analysis; "classical" methods of uranium analysis such as volumetry or spectrophotometry have been greatly improved by the introduction of new reagents and better instrumentation.

The mineralogist and the geochemist exploring the uranium resources of our planet urgently need rapid, cheap, sensitive, specific and reliable analytical tools for the determination of minute amounts of uranium in their samples. In certain cases the use of suitable instruments in the field is desirable, e.g. the apparatus should be easily transportable.

For the first mapping of uranium occurrences, gamma-surveymeters and instruments based on radon measurements may be used.

The principal part of the gamma-radiation from a uranium mineral is emitted by 226 Ra and its decay products. A surveymeter will also register the gamma-radiation from thorium decay products and from potassium, but by having separate energy "channels" an individual evaluation of uranium + radium, thorium and potassium contributions is possible. Determination of the radioactive disequilibrium

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between radium and uranium in a sample and hence the determination of uranium concentration is difficult, however. Radon measurements again only show the radium content of the uranium bearing material without providing information on the effective equilibrium of uranium to radium.

The advantage of the methods given above is their rapidity, which makes possible a scanning of wide areas in a relatively short time, especially when air-borne gamma--scintillometers permitting energy discrimination are used, which are able to distinquish between the individual natural gammaemitters. But after the radiation contour mapping samples must be taken and analysed for uranium by several methods to obtain more accurate and precise information about the true uranium content of the individual specimen.

A direct specific gamma measurement of uranium correcting for not too extreme disequilibrium conditions in the minerals was developed by Suschny (1976), it only requires the availability of a multichannel-analyser. The method is in routine use in this laboratory.

Methods measuring ^{235}U or ^{238}U directly do not depend on knowledge of the disequilibrium in the decay series. The natural ratio of this two uranium isotopes is generally assumed to be constant (some exceptions are possible). The fission of

Table 1

Detection limits and precision of some methods suitable for the determination of microamounts of uranium

Method	Detection limit	Precision at 10× detection limit
Conventional fluorimetry (solid samples)	0.1—0.2 ppm	±25%
Laser fluorimetry (waters)	0.1—20 ppb	±15—20%
Neutron activation analysis (sediment samples)	1 ppm	variable
Delayed neutrons	0.1 ppm	±10—15%
X-ray fluorescence	variable	variable

^{235}U with thermal neutrons (fast fission of ^{238}U and ^{232}Th is usually negligible) is the basis of the "fission track", the fission product" and the "delayed neutron" methods, which are very sensitive and highly specific, but require a nuclear reactor and some expensive instrumentation. The fission track method should not be confused with the "track-etch" technique for radiation mapping in uranium exploration; the basis of the latter method is the registration of the underground alpha-radiation from radon and its daughter products by a suitable photographic film.

The measurement of small amounts of ^{238}U is possible, when the sample is irradiated with the thermal or epithermal ("epicadmium") neutrons from a nuclear reactor (to obtain sufficient sensitivity), the use of epithermal neutrons improves the ratio of uranium and unwanted radiation from other mineral constituents. The uranium may be measured as ^{239}U or its immediate decay product ^{239}Np:

$$^{238}_{92}(Un,\gamma)\ ^{239}_{92}U \xrightarrow[23.5\ min]{\beta} {}^{239}_{93}Np \xrightarrow[2.3\ days]{\beta} {}^{239}_{94}Pu$$

An other very sensitive method for the determination of uranium is liquid scintillation counting (Bouwer et al. 1978). The authors of the most sensitive version of this methodology claim a detection threshold of 0.004 ppm of uranium (Bouwer et al., 1978), but this technique requires a special electronic system, the chemical procedure involved appears rather time-consuming and the alpha-resolution is a poor one. The high sensitivity of this method makes it potentially useful for special purposes; it was originally developed for the determination of uranium in phosphate fertilizers and phosphatic minerals.

In contrast to the methods mentioned above (and some others) conventional as well as laser fluorimetry combine specifity, high sensitivity (see table 1), relatively simple equipment, the possibility of field use and reliability with rapidity at rather low costs.

HISTORICAL BACKGROUND

The element uranium, discovered in 1789, shows in its hexavalent form an intensive yellowish-green fluorescence, when irradiated with UV-light or cathode-rays. This fluorescence was observed by Stokes (1852) and Becquerel (1859). It represents the basis of a very sensitive method for the microdetermination of uranium, which is called fluorimetry. It should be noted here, that one of these authors, Edmond Becquerel, was the father of Henri Becquerel, who has discovered radioactivity in the course of his investigation of uranium fluorescence, which lead consequently to the famous discovery of polonium and radium by Maria Sklodowska-Curie and her husband Pierre.

In our century (1926) it was discovered, that the uranium fluorescence is greatly intensified by the embedding of the uranyl-compound in various matrix systems, preferably fluorides such as sodium fluoride (Nichols, Slattery 1926); the fluorescence of uranium in NaF was easily detected at a ratio U:NaF$\cong$1:10^7! This observation has been utilized by some authors (Papish, Hoag 1927; Hernegger 1933) for the development of a very sensitive qualitative test for uranium: the mineral powder was touched with a pearl of fused sodium fluoride in a platinum wire loop, followed by a second fusion. After cooling the mineral powder dissolved in NaF was irradiated with UV-light; a yellowish-green fluorescence showed the presence of uranium.

At the beginning of the fourth decade of our century geochemists became interested in the uranium content of sea-water, but no method of sufficient sensitivity existed for its determination. For that reason the qualitative fluorimetric test for uranium was developed into a quantitative method (Hernegger, Karlik, 1935). The uranium was separated from the sea-water by a classical chemical separation scheme, which was mainly based on the "carbonate separation" of UO_2^{2+} and Fe^{3+}. The first results obtained showed contents between 3.6×10^{-7} and 3.37×10^{-6} g uranium per liter of sea water.

The fluorimetric technique suffers from a principal drawback: the reduction of the uranium fluorescence in the presence of interfering elements. This phenomenon is called the "quenching effect" and the corresponding elements "quenchers".

The above mentioned effect has been often studied since the beginning of quantitative fluorimetry. It will be treated in more detail in the next part.

It should be also mentioned here, that crystals containing U, Th or an other radioactive element are subject of irradiation by the radiation originating from the ra-

dioactive substance (alpha-, beta-, gamma-radiation). A part of the radiation energy is deposed in the crystals via various processes and may give rise to a luminescence effect, but this has nothing to do with uranium fluorimetry.

THE QUENCHING EFFECT AND ITS ELIMINATION

The definition of quenching

The quenching effect is defined as the reduction of the fluorescence light intensity (which is probably coupled with a shift in the wavelength of the emitted light) by the presence of interfering substances. The "degree of quenching" is given by:

$$Q = 100 \times \left(1 - \frac{I}{I_o}\right)$$

I_o=unquenched fluorescence light intensity,
I=quenched fluorescence light intensity.

Many elements may cause a more or less massive quenching of the uranium fluorescence, for example Mn, Cu, Cr, Fe, Ni, Co and many others. The quenching power of a given element is one of its individual properties and may be expressed by its "half contentration" $c_{1/2}$, e.g. that quantity of an element, which reduces the unquenched fluorescence of the uranium by 50%. This term has been introduced via theoretical considerations in 1945 by Price et.al. and was thoroughly studied experimentally in recent years (Veselsky and Ratsimandresy 1979, Veselsky 1981a, b). It turned out, that in the generally used "conventional" fluorimetry (e.g. the measurement of the uranium fluorescence excited by the radiation of UV-lamps in solid flux pellets) the quenching effect obeys up to a certain limit (wchich is around 55—60% quenching) a semilogarithmic law i.e. the dependance of the quenching effect on the concentration of the quencher is semilogarithmic (see Fig. 1).

$$I = I_o \cdot e^{-k \cdot c}$$

I_o — unquenched fluorescence light intensity,
I — quenched fluorescence light intensity,
k — constant,
c — concentration of the quencher in the flux pellet (usually in ppm).

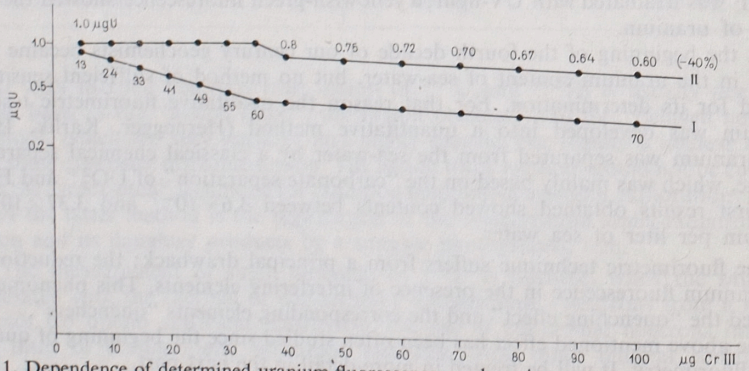

Fig. 1. Dependence of determined uranium fluorescence on chromium concentration in the sample
Curve I — without correction; the figures below I mean % of quenching. Curve II — after correction by the internal standard method

This law is a formal analogon to the widely used law of Lambert and Beer (in spectrophotometry) as well as to the law of radioactive decay. From the latter law the important term "half-life" may be easily derived, the same is possible with the basic law of quenching:

$$c_{1/2} = \frac{\ln 2}{k}$$

This term $c_{1/2}$ may be used for the precise classification of quenchers. Definitions of quenchers such as "moderate", "weak" or "strong quencher", which may be encountered in literature, are imprecise and must be considered as outdated. Some of the more important quenchers and their $c_{1/2}$ values are listed in table 2. For a more detailed list see Veselsky (1981b) and also for the quenching behaviour of binary mixtures.

Table 2

The half-concentrations of some important quenchers (Veselsky 1981b)

Quencher	Mn(II)	Co(II)	Cr(III)	Fe(III)	Cu(II)	Ni(II)
$c_{1/2}$ (ppm)	16	19	40	64	81	125

The highest "quenching power" and therefore the lowest half-concentration known is shown by manganese. For this reason a simple and reliable method has been developed to remove this element from sample solution by precipitation with sodium bromate. The element iron in turn, due to its relatively high quenching power in combination with its high concentration in many minerals must also be considered as "dangerous" in fluorimetric uranium analysis. With high uranium concentrations in the pellets a self-quenching effect may occur.

Elimination of quenching

The methods available for elimination of the quenching effect may be subdivided into three groups: compensation, dilution and separation methods.

The compensation technique is mainly represented by the "internal standard" or "spike" method. It makes use of the fact that quenching is only dependant on the absolute concentration of the quencher in the flux pellet and not on the ratio uranium: quencher (Veselsky 1981a). With this method a known amount of uranium is added to the measured flux pellet, followed by another fusion process and subsequent measurement. The true uranium content of the pellet is calculated using the following formula:

$$\mu g\ U = \frac{I_1 \cdot \mu g\ S}{I_2 - I_1}$$

I_1 — fluorescence of sample,
I_2 — fluorescence of sample + internal standard,
µg S — µg U added as internal standard,
µg U — µg U originally present in the pellet.

For examples concerning this method see Schönfeld et al. (1960), Veselsky and Wölfl (1976). It is only applicable up to a quenching of the uranium fluorescence of about 55—60%, i.e. up the limit of the regular part of the quenching function.

The "dilution" method is based on the fact, that with the dilution of a mixture of quenchers and uranium (for example solutions of natural minerals) the quenching

effect disappears much more rapidly than the uranium fluorescence diminishes. The dilution may be carried out in solution as well as in the solid flux pellet; i.e. by the use of bigger pellets. Examples for the use of this method may be found in papers of Smith et al. (1973) and Suschny (1975).

A special case of the dilution technique is the "extrapolation method", it is based on the linearity of the semilogarithmic quenching function at relatively low sample concentrations. Small, but different quantities of the finely powdered sample are fused with flux mixture and measured; the relative fluorescence intensity per unit of sample weight is calculated and plotted against the sample weight on semilog paper. Linear extrapolation of the quenching function to sample weight zero yields the true, unquenched sample fluorescence (Veselsky, Ratsimandresy 1979). This method also is only applicable as long as the linear function is valid (see Fig. 2).

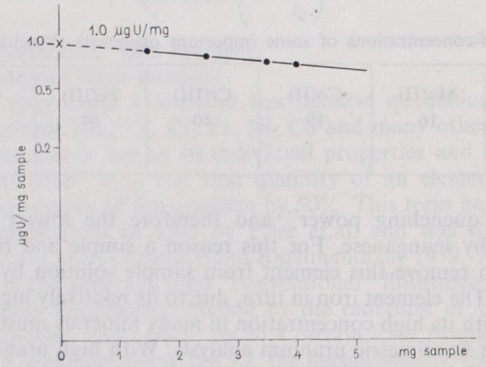

Fig. 2. The extrapolation method

Widely used methods for elimination of quenching are based on the separation of uranium from the matrix (geological samples, water). These separations may be carried out by precipitation (Kim and Zeitlin 1971), chromatographic methods (Grimbert and Berthollet 1959), ion exchange (Korkisch et al. 1977; Burba et al. 1978) or solvent extraction using diethyl ether, ethyl acetate, methyl isobutyl ketone (MIBK, Hexone), phosphoric acid esters such as tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO) or amines such as trioctyl amine (TOA), Alamine 336 and others. This type of separation may be carried out as conventional extraction or as extraction chromatography (Centanni et al. 1956, Maeck et al. 1958, Wódkiewicz 1961, Schieferdecker 1968, Kim and Zeitlin 1971, Korkisch and Koch 1973, Veselsky et al. 1974, Strain 1978).

FLUORIMETERS AND FLUORIMETRIC TECHNIQUES

A fluorimeter usually consists of a source of ultraviolet radiation (mercury lamp, black light emitter), a filter system for the isolation of the uranium fluorescence radiation, a conversion unit (usually a photomultiplier) and an instrument for the measurement of the photocurrent (microamperometer or digital display). The fluorimeters may be of the "reflectance" or the "transmission" type. The schematic cross sections of two fluorimeters of the "reflectance" type are given in Figs. 3 and 4.

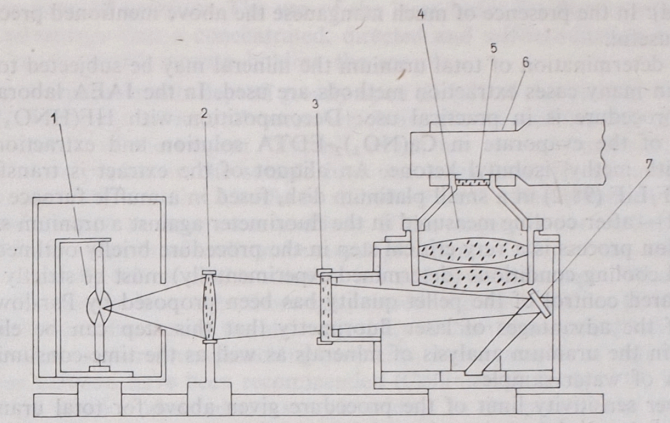

Fig. 3. Conventional fluorimeter with mercury lamp (old model)
1 — UV source, *2* — focusing lens, *3* — primary filter, *4* — focusing lens system, *5* — secondary filter, *6* — photomultiplier, *7* — sample

The instrument shown in Fig. 4 is used in the IAEA laboratory and proved reliable. An advanced model of fluorimeter has been developed by Müller and Ross, described in Strain's paper (1978). This apparatus is fully transistorized, the calibration curve is generated internally and there is a digital readout in nanograms of uranium. A modern type of transmission fluorimeter has been developed by Parslow (1979).

According to the aims of the analysis different methods for the determination of uranium in minerals and waters are in use. For the assay of various uranium fractions of the corresponding mineral substance several extraction techniques are in use, (i.e. "Extractable" or "leachable" uranium). Leaching procedures with 4M HNO_3 or HNO_3—HCl mixtures or other extractants are described by Smith and Lynch (1969) and Suschny (1975).

A fraction of the extract is directly evaporated in a platinum dish, fused with an appropriate flux (Na_2CO_3(K_2CO_3)NaF in proportion 45.5/45.5/9) and after cooling measured in the fluorimeter against a known uranium standard; quenching effects are reduced by the use of big flux pellet ("dilution method"). In the case of very high quenching a separation method may be used ("combined method" — Veselsky

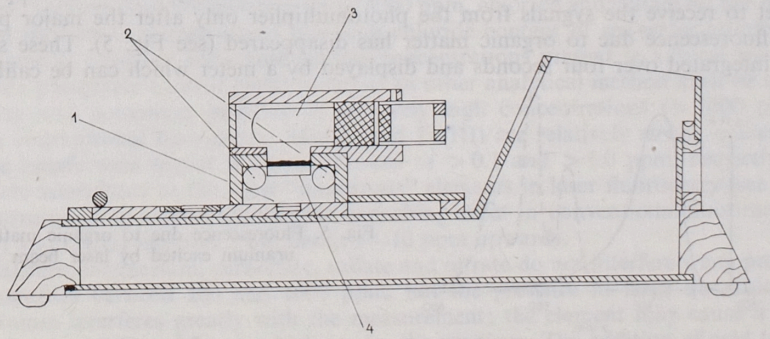

Fig. 4. Galvanek Morrison fluorimeter
1 — sample slid, *2* — UV "Black light" lamps, *3* — photomultiplier, *4* — secondary filter system

unpublished). In the presence of much manganese the above mentioned precipitation process is useful.

For the determination of total uranium the mineral may be subjected to various treatment, in many cases extraction methods are used. In the IAEA laboratory the following procedure is in practical use: Decomposition with $HF(HNO_3)HClO_4$, dissolution of the evaporate in $Ca(NO_3)_2$-EDTA solution and extraction of the uranium with methyl isobutyl ketone. An aliquot of the extract is transferred to 400 mg NaF/LiF (98/2) in a small platinum dish, fused in a muffle furnace at about 1000°C and — after cooling measured in the fluorimeter against a uranium standard.

The fusion process is a very critical step in the procedure briefly outlined earlier, heating and cooling conditions (determined experimentally) must be strictly adhered to. An infrared control of the pellet quality has been proposed by Parslow (1979). It is one of the advantages of laser fluorimetry that this step can be eliminated completely in the uranium analysis of minerals as well as the time-consuming total evaporation of water samples.

The lower sensitivity limit of the procedure given above for total uranium determination is in our laboratory about 0.3 ppm of uranium in the mineral.

LASER FLUORIMETRY

The principles of the determination of uranium in solution by laser fluorimetry may be described in brief as follows; as model apparatus the uranium analyser UA-3 of Scintrex was taken (Scintrex 1978).

Instead of mercury or black light lamps as they are used in conventional fluorimeters the uranium fluorescence is excited by a monochromatic UV beam ($\lambda =$ $= 337.1$ nm) from a pulsed nitrogen laser (15 pulses per second). The "illumination time" is very short ($3—4 \times 10^{-9}$ seconds) and not only the uranium fluorescence is excited, but also a blue radiation (maximum around 400 nm) originating from the organic material dissolved in most of the water samples (concentrations < 1— —30—40 mg/liter). This radiation can be blocked by the use of green filters, but longer wavelengths may be transmitted and interfere with the uranium fluorescence whose main peaks are located at 494, 516 and 540 nm (Robins, 1978). This latter effect can be greatly reduced by time discrimination: the half-life of the fluorescence from organic substances is only some 10^{-10} seconds, that of the uranium fluorescence considerably longer (10^{-7} seconds); the electronic system of the apparatus is set to receive the sygnals from the photomultiplier only after the major part of the fluorescence due to organic matter has disappeared (see Fig. 5). These signals are integrated over four seconds and displayed by a meter which can be calibrated

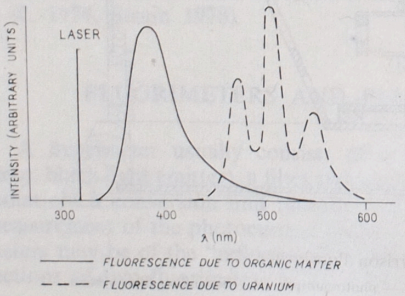

Fig. 5. Fluorescence due to organic matter and uranium excited by laser beam

directly in ppm of uranium. The use of the laser beam for fluorescence excitation has the advantage that a concentrated, directed and self-terminating beam can be focused in the quartz cuvette holding the sample.

Good analytical results depend greatly upon the pH of the sample, which should be 5.5—7; in the case of natural waters which are not yet acidified this may be obtained by addition of the reagent "fluran", which has several functions: it converts all UO_2^{2+}-ions present in the sample into one single complex compound of high luminescence yield, contains a buffer to stabilise the pH of the solutions and is masking quenchers such as manganese and iron. If the reagent is not available, it can be replaced by a solution of sodium hexametaphosphate (7.4 g of the salt in 100 ml of water), usually 0.8 ml of this solution are added to the sample. When using this reagent, the cuvettes have to be thoroughly rinsed with dilute HCl or HNO_3, followed by distilled water. Because of the high sensitivity of this method the dilution technique is widely used to overcome quenching problems, water samples of only 10 µl diluted to various volumes have been recommended (Collins and Zook 1979, White 1980); such a high dilution also reduces sample acidity. In the presence of much organic material, the fluorescence needs some time for "development", this interval represents the time which is necessary to liberate the UO_2^{2+} ions from their original organic complexes and bind them to the complexing agent delivered by the fluran reagent.

Water samples sent from the field to the laboratory are usually acidified and must be neutralized (if they cannot be suitably diluted) prior to the measurement if the acid concentration exceeds 0.1%, to ensure a proper pH. Any particulate matter suspended in the water sample must be removed by filtration. It is not advisable to simply add a standard quantity of base to the acidified sample because of the variable buffer capacity of natural waters, but the pH should be checked after the uranium measurement, if it is < 5.5 — the analysis must be repeated with a fresh sample whose pH was adjusted to about 5—6 by titration with sodium hydroxide.

Campen and Bächmann (1979) have investigated various aspects of the laser fluorimetric methodology: the dependance of the analytical results upon the quantity of fluran addition, the temperature of the cuvette and the influence of various anions and cations. Their results may be discussed briefly:

1. The fluorescence is initially increased with increasing fluran addition, from a certain point it remains constant.
2. The signal intensity decreases with increasing temperature.
3. The signal remains constant up to about 1000 ppm of carbonate, then it decreases. Sodium does not interfere up to 4000 ppm, chloride and sulfate do not interfere at moderate concentrations (the high chloride content of sea-water interferes). The same is valid for phosphate (at low concentrations present in natural waters), for high phosphate content (solid samples) an other analytical method must be used. Sodium and potassium interfere at relatively high concentrations (> 1000 ppm). As in conventional fluorimetry, Mn(II) and Fe(III) are relatively strong quenchers whose interference begins at concentrations of > 0.1 and > 1.0 ppm, respectively; they are considered as the most "dangerous" elements in laser fluorimetry (see also the corresponding section treating the quenching effect in conventional fluorimetry). Ni(II) and Cu(II) interfere from about 1—10 ppm upwards.

Calcium, magnesium, carbonate, sulfate and nitrate do not interfere when present in quantities between 100 and 1000 ppm, but the presence of large quantities of aluminium interferes greatly with the measurement: the element may cause a precipitate on addition of fluran which carries the uranium. The addition of acid to redissolve the precipitate affects the result of the analysis, a dilution of the sample

may be tried, but in this case the uranium concentration may drop below the detection limit and other method must be used. Similar problems are encountered with acid extracts of minerals: a dilution technique and internal standards for the compensation of the matrix effects may have to be used. In general, the determination of uranium in minerals with laser fluorimetry is much more difficult than the detection in water.

When the internal standard method is used, the following formula may be applied for the calculation of the results:

$$Z = \frac{v_1}{v_2 - v_1} \cdot \frac{a}{b} \cdot U$$

Z = ppb uranium in sample solution,
v_1 = meter reading from sample,
v_2 = meter reading from sample + internal standard,
a = volume of standard edition (ml),
b = volume of sample (ml),
U = concentration of uranium standard solution (ppb).

A methodology for the determination of uranium in process water, including a detailed working procedure, using a laser fluorimeter was described by White (1980). This author has also found interfering effects from Mn, Mg and Ca caused by the reduction of the fluorescence life-time and quenching effects due to the absorption of fluorescence light in the presence of Fe(III) and humic acids. High calcium and magnesium concentrations may also result in the formation of a precipitate with the addition of fluran, but a redissolution is possible by the addition of a drop of 85% phosphoric acid; standard addition is also recommended. The presence of phosphate in the sample may cause fluorescence before the addition of fluran (White, 1980).

Tikoo and Murty (1980) have used fluorimetry for the determination of uranium in water and geological samples, the latter were dissolved by a HF/HNO_3 treatment followed by sodium peroxide fusion of the residue. They have found that Na, K, Mg, NO_3^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-} do not interfere with the determinations. Mc Hugh (1982) has decomposed mineral samples by KOH fusion and separated the uranium by ethyl acetate extraction.

A method for the determination of the uranium content in plant material by laser fluorimetry was developed by Harms et al. (1981). The plant tissue is ashed at 450°C and the residue treated with 2.5M HNO_3 saturated with aluminium nitrate. The uranium is extracted from the solution with ethyl acetate, the solvent boiled off, the residue ignited and then taken up in 0.005% nitric acid. This solution is measured in the laser fluorimeter; the sensitivity of the method is given as 0.05 ppm uranium in plant ash.

For the determination of microamounts of uranium in solution using a dye-laser excited by a pulsed nitrogen-laser it is worth to see a paper of Kenny-Wallace et al. (1981), for a laser fluorimetric method achieving a detection limit of 10^{-5} ppb U (0.01 pg) — Perry et al. (1981). Johnston and Wright (1981) have developed a methodology using co-precipitation of uranium with calcium fluoride and measuring the fluorescence of the solid CaF_2 body excited by a UV laser beam, with a detection limit of 0.4 pg U/ml.

In the IAEA laboratory an improved method has been developed for the analysis of minute amounts of uranium in minerals using laser fluorimetry (Veselsky et al., to be published). The technique was tested with the aid of conventional fluorimetry. A total of sixty samples has been analysed using six mineral powders of very different

Table 3

The analysis of six different mineral samples for uranium using conventional and laser fluorimetry. The results are given in ppm throughout

Sample No.	Conventional fluorimetry	Laser fluorimetry
1. Jasperoid reefs	23.7±4.3	25.5±4.1
2. Residual loam	1.8±0.3	1.8±0.3
3. Fe—Mn—W—rich hot spring deposit	1.5±0.6	1.7±0.6
4. Porphyry cooper ore	4.5±0.4	5.9±1.0
5. Podzolic soil	1.3±0.2	1.6±0.4
6. Residual yellowish-red soil	0.8±0.1	1.2±0.3

origin and composition. The results are given in table 3. The details of the method will be published in a special juornal for analytical chemistry.

It may be said that laser fluorimetry, which represents the "ideal" method for determination of uranium in natural waters, will in future play a role of increasing importance also for minerals. The method is very sensitive, specific, rapid and the technician performing the analyses must not be as skilled as it is required for conventional fluorimetry. The apparatus is not too big (dimensions 30×38×45 cm) or heavy (approximately 15 kg) and it is portable, suitable for both field and laboratory applications. The operation temperature of the laser fluorimeter is given by the manufacturer as −10 to +40°C (Scintrex, 1978). Some of the intermediate steps of the UA-3 fluorimeter method can be easily improved in future.

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FLUORYMETRYCZNE OZNACZANIE URANU W MINERAŁACH I W WODZIE ZE SZCZEGÓLNYM UWZGLĘDNIENIEM FLUORYMETRII LASEROWEJ

Streszczenie

W pracy przedstawiono rozwój metod fluorymetrycznych stosowanych do oznaczeń zawartości uranu. Wyjaśniono rolę i znaczenie substancji wygaszających efekt fluorescencji, tzw. interferentów. Zaprezentowano nową koncepcję funkcji wygaszania. Przedyskutowano zarówno pozytywne jak i niekorzystne aspekty klasycznej fluorymetrii. Opisano szczegółowo nowoczesną, udoskonaloną metodę fluorymetrii z zastosowaniem lasera i podkreślono jej zalety. Przedstawiono wyniki oznaczeń zawartości uranu (w ppm) w próbkach mineralogicznych wykonane przy zastosowaniu obu technik: klasycznej (konwencjonalnej) i laserowej fluorymetrii.

OBJAŚNIENIA FIGUR

Fig. 1. Zależność fluorescencji uranu od koncentracji chromu w próbce
Krzywa *I* — bez korekty, krzywa *II* — po korekcie metodą standardu wewnętrznego. Liczby oznaczają wygaszanie w procentach
Fig. 2. Metoda ekstrapolacji dla określonego stężenia uranu w próbce
Fig. 3. Konwencjonalny fluorymetr z lampą rtęciową (stary model)
1 — źródło światła ultrafioletowego, *2, 4* — soczewki ogniskujące, *3, 5* — filtry (pierwotny i wtórny), *6* — fotopowielacz, *7* — próbka
Fig. 4. Fluorymetr firmy Galvanek-Morrison
1 — próbka, *2* — źródło światła ultrafioletowego, *3* — fotopowielacz, *4* — filtry
Fig. 5. Wykres fluorescencji materii organicznej i uranu wzbudzonej wiązką lasera

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DIE FLUORIMETRISCHE BESTIMMUNG DES URANS IN MINERALEN UND WASSER UNTER BESONDERER BERUECKSICHTIGUNG DER LASER-FLUORIMETRIE

Zusammenfassung

Ein Überblick über die konventionelle Uranfluorimetrie wird gegeben. Die Rolle störender Stoffe („Löscher") wird beleuchtet und es werden Methoden angegeben, wie diese Schwierigkeiten überwunden werden können. Das neue Konzept der „Löschfunktion" wird etwas ins Einzelne gehend diskutiert. Vor- und Nachteile der klassischen Uranfluorimetrie werden dargelegt. Im zweiten Teil der Arbeit wird die verbesserte fluorimetrische Bestimmung des Urans in Mineralen unter Verwendung eines Lasergeräts im Prinzip erklärt, einige praktische Arbeitsverfahren werden erwähnt sowie Resultate einer eigenen Entwicklung aufgezeigt.

TITEL DER ABBILDUNGEN

Fig. 1. Abhängigkeit der gemessenen Uranfluoreszenz von der Chromkonzentration in der Probe
Kurve I — ohne Korrektur, die Zahlen unterhalb der Kurve geben den Löscheffekt in %. Kurve II — nach Korrektur durch den internen Standard

Fig. 2. Die Extrapolationsmethode

Fig. 3. Konventionelles Fluorimeter mit Quecksilberlampe (altes Modell)
1 — UV-Quelle, *2* — Fokussierende Linse, *3* — Primärfilter, *4* — Fokussierendes Linsensystem, *5* — Sekundärfilter, *6* — Sekundärelektronenvervielfacher, *7* — Probe

Fig. 4. Galvanek-Morrison Fluorimeter
1 — Beweglicher Probenbehälter, *2* — UV Schwarzlichtlampen, *3* — Sekundärelektronenvervielfacher, *4* — Sekundärfiltersystem

Fig. 5. Fluoreszenz von organischen Stoffen und Uran, angeregt durch einen Laserstrahl