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BEHAVIOUR OF INDIUM AS A TRACER FOR KARST WATER RESEARCH

BY

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The authors present the results of a two-year research on using indium in the form of the In-EDTA complex as an activable tracer in hydro-karst studies.

1. INTRODUCTION

Tracers have been used in hydrokarst studies for quite a long time, owing to the progress made in speleology. However, whereas in any other hydrological field, tracer methods can be replaced by other convenient procedures, in karst hydrology they are peremptory because of the spectacular results thus obtained. An examination of many tracer activities carried out at home and abroad, in this field as well as in tracer data processing and a better over-all knowledge of karstic aquifers and their hydrodynamics allows us to outline the efficiency, limits and prospects of tracers' use in karsts.

Results of the early In-EDTA labellings conducted in several karst areas in Romania were reported at last year's session of this symposium (Gaşpar, 1984 ; Ponta, 1984 ; Orăşeanu, 1984).

After a two-year labelling of various hydrokarst structures, for which the flow rate and transit time parameters assumed a wide range of values, we are finally in a position to draw some conclusions on the behaviour of this tracer.

2. METHOD

Basically, this method emploing In as an activable tracer in the form of the In-EDTA complex consists in labelling an input by use of a δ pulse, whereupon water samples of about 250 to 500 ml are collected from the emergences at specified time intervals. The tracer can be separated and measured in compliance with Behrens' method (Behrens, 1977), which has the following inconveniences :

— the samples prepared for activation analysis are rather bulky, and so the number of simultaneously irradiated samples is restricted ;

— the samples incorporate a large amount of air which, upon irradiation yield ^{41}Ar which must be removed after wards ;

— clean filters are required so as to prevent the formation of gamma emitters induced by neutron irradiation.

The method used by the authors (Stănescu, 1982) is free of such inconveniences. Thus, to remove In, the samples containing 100 ml water are subjected to co-precipitation with bismuth hydroxide ; then, to eliminate all errors and disturbances caused by the nature of the filter, the water containing the precipitate is filtered under pressure on a nuclear membrane filter by use of a forevacuum pump. After drying at room temperature, the precipitate is removed from the filter and then encapsulated warm in polyethylene sheets.

Polyethylene capsules containing the precipitate in the form of In and Bismuth hidroxide powder are activated by neutron irradiation at a pneumatic tube of the nuclear reactor, together with the reference sample, and the intensity of the 417 keV gamma radiation is measured. Then the amount of In concentration in water is found by means of the following relation :

$$C = \frac{C_e \cdot A \cdot (1 - e^{-\lambda \cdot t_e}) \cdot e^{+\lambda \cdot t_r}}{A_e \cdot (1 - e^{-\lambda \cdot t})}$$

where :

— $\lambda = 0.012833 \ \mathrm{min}^{-1}$;

— C, C_e are the indium concentration in the experiment sample and in the reference sample, respectively ;

— t, t_e denote the measuring time of the experiment sample and reference sample, respectively ;

A, A_e represents the net area of the photopeak corresponding to the gamma radiation of 417 keV for the experiment sample and reference sample, respectively (fig. 1) ;

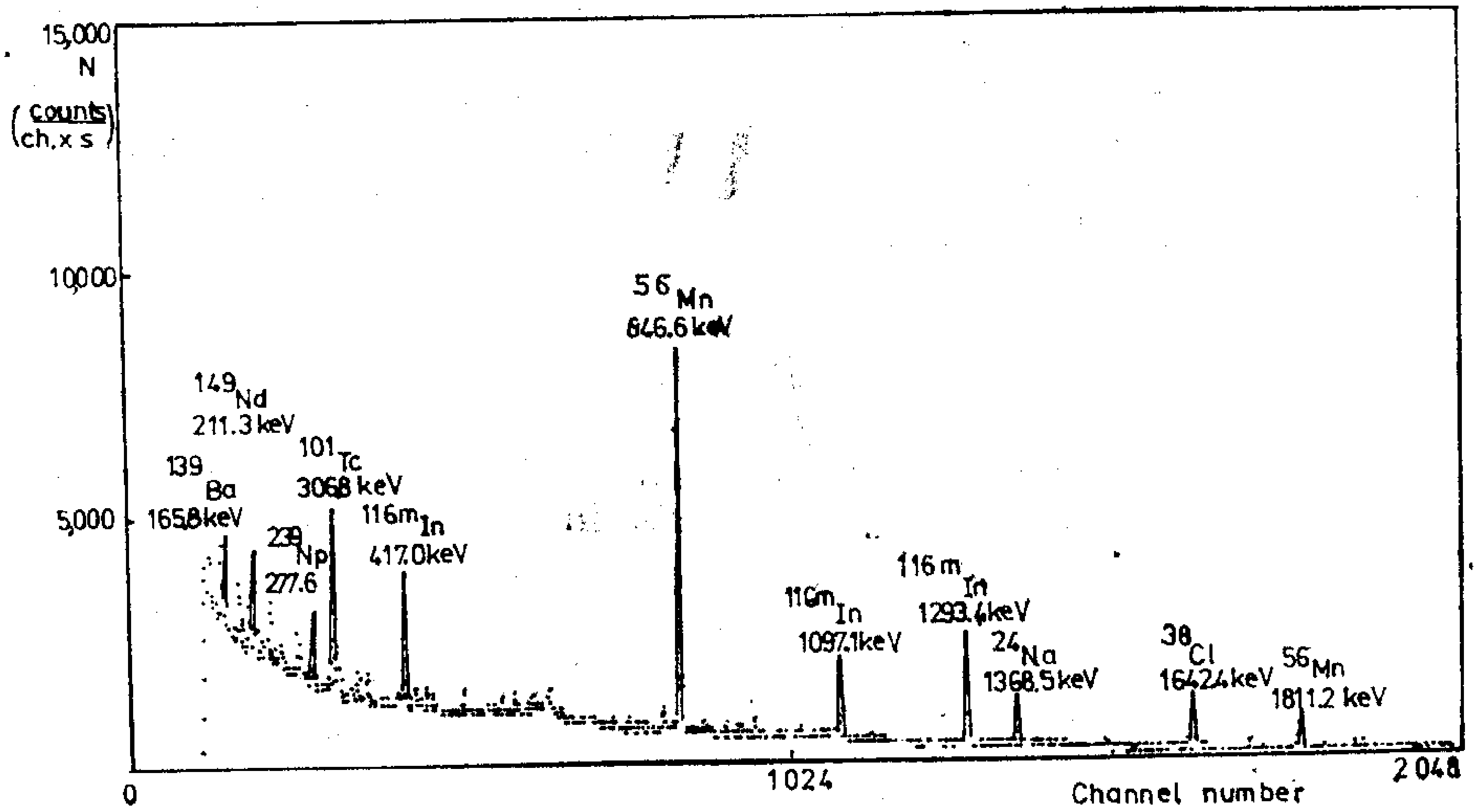

Fig. 1. Gamma-ray spectrum of a water sample containing Indium.

— t_r is the time interval between experiment sample measurement and reference sample measurement.

Since non-filter samples are smaller, several such samples can be irradiated smultaneously using a pneumatic tube system of small diameter, and ^{41}Ar contamination occurs no longer.

3. INDIUM AMOUNT FOR ONE LABELLING

The main advantage of this tracer is that owing to its extremely low detectability limit, it can label limmergences of very low flow rate which could not be labelled by any other tracer, fluorescent, chemical or radioactive except for tritiated water, HTO).

From the labelling works carried out in 1982 and 1983 the following empirical relation,

$$M_0 = Q \cdot T \cdot P \cdot K,$$

was derived, where M_0 is the In amount (in g) required for one labelling, Q is the sum (m^3/s) of flow rates of the emergences where the tracer might occur, T is the time interval (in days) estimated by the experiment author for the tracer to pass through the observation point and for a value of at least 10 for the maximum / minimum concentration ratio, P is a loss coefficient expressed by the M_0/M ratio, where M is the In amount recovered, and K is a safety coefficient. Use of coefficient P is justified since some amount of the tracer may be retained in the sub-systems during drought periods, while for long transit times, part of the tracer may be lost in various traps. A value of 1 . . . 3 is thought to be resonable for

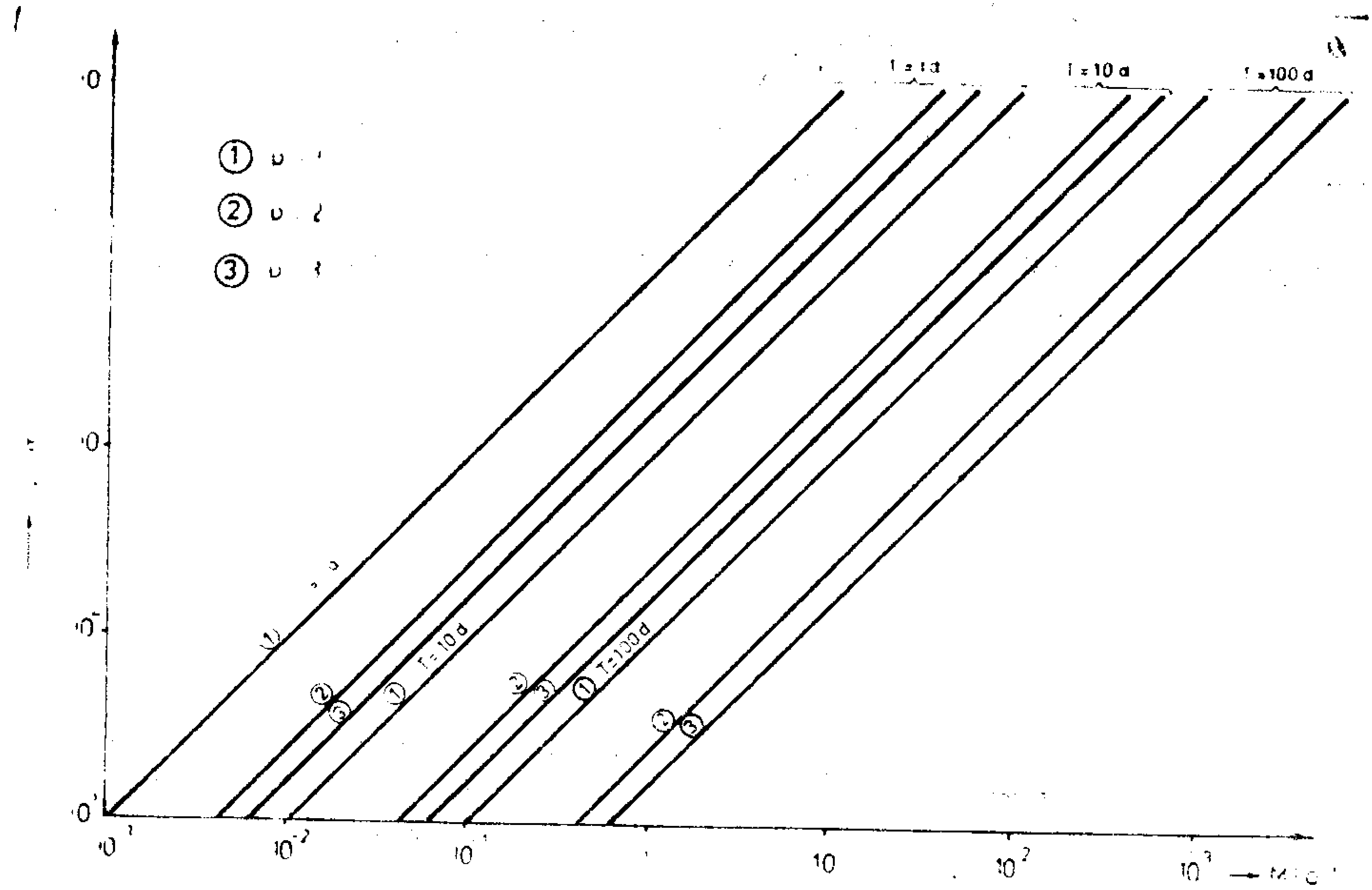

Fig. 2. Indium amount for one labelling diagram.

this coefficient. As for the K-coefficient, its value did not exceed 2 in our experiments.

Figure 2 shows a diagramatic representation of the relation for several ordinary values.

4. INDIUM BEHAVIOUR IN HYDROKARST ENVIRONMENT

In the years 1982—1984, labellings were conducted in various hydrokarst structures. As the aim pursued in this experimental labellings was to test a new tracer, it was desired that a minimum amount should be used. This idea was founded on two reasons: on the one hand, this allowed for an effective investigation on In's behaviour in the underground, while, on the other hand, the use of large concentrations could have caused a contamination of the test laboratory that would have largely influenced further determinations.

The 15 labellings conducted are presented in Table 1, and Figs. 3—6 show the trrnsfer curves for some labellings. In this table, t denotes the average transit time, given by the following relation:

$$t = \frac{\int_0^\infty C(t) \cdot t \cdot dt}{\int_0^\infty C(t) \cdot dt}$$

It should be mentioned that all of the labellings performed during the 1982—1984 period led to positive results.

In general, underground tracer retention due to physical or chemical processes was not significant. The tracer amount recovered was satisfactory in most of the experiments. An accurate evaluation of the amount recovered requires continuous measuring of flowrates and concentrations, which is rather difficult to achieve over a longer time interval, as

$$M = \int_0^\infty C(t) \cdot Q(t) \cdot dt$$

The ratio of the tracer amount injected, M_o, to the tracer amount recovered, M,

$$P = \frac{M_0}{M}$$

is found to be smaller than 3. Tracer loss is generally due to retention in the sub-systems. Thus, for instance, at the Cerna Spring (fig. 3), the flowrate went constantly down throughout the measuring period, and this indicates that plashes had been left acting, as traps for the tracer in some free-flow portions of the under-

Table 1

Appearance and Concentrations of In-EDTA in Springs

No. Karstic drainage	Flow rate of emergences, l/s	Amount injected g	First appearance after injection	Appearance of maximum	Maximum concentration 10^{-11} g/cm^3
1. Doboș-Toplița de Roșia	50	0.7	36 h	50 h	16
2. Valea Luncilor-Brătcani	100— 220	15	2 d	3 d	13.8
3. Bichii swallet-Vida	25—1500	10	40 d	60 d	0.94
4. Scorota swallet-Cerna spring	840—2730	100	12 d	13 d	7
5. Motru Sec-Bolboros	110	65	6 d	8 d	38
6. Tomii swallet-Izbîndiș	170	13.6	32 d	34 d	2.84
7. Barc swallet-Roșia	105— 200	14.5	26 d	28 d	0.78
8. Valea Peștișului-Aștileu	70	17.1	90 d	100 d	2.28
9. Valea Poenii-Aștileu	65	20	30 d	32 d	4.84
10. Valea Corlatului-Criș River Spring	100	4	31 d	35 d	3.06
11. Baia Nițului-Toplița de Vida	65	20	54 d	60 d	1.63
12. Bistrița-Izvarna	2000	84	9 d	10 d	3.9
13. Valea Pîrgavului-Izvarna	2000	65	10 d	12 d	1.8
14. Sabar-Sabar	25	0.07	70 min	80 min	162
15. Măcîrlău swallet-Măcîrlău river	150	40	20 h	54 h	63

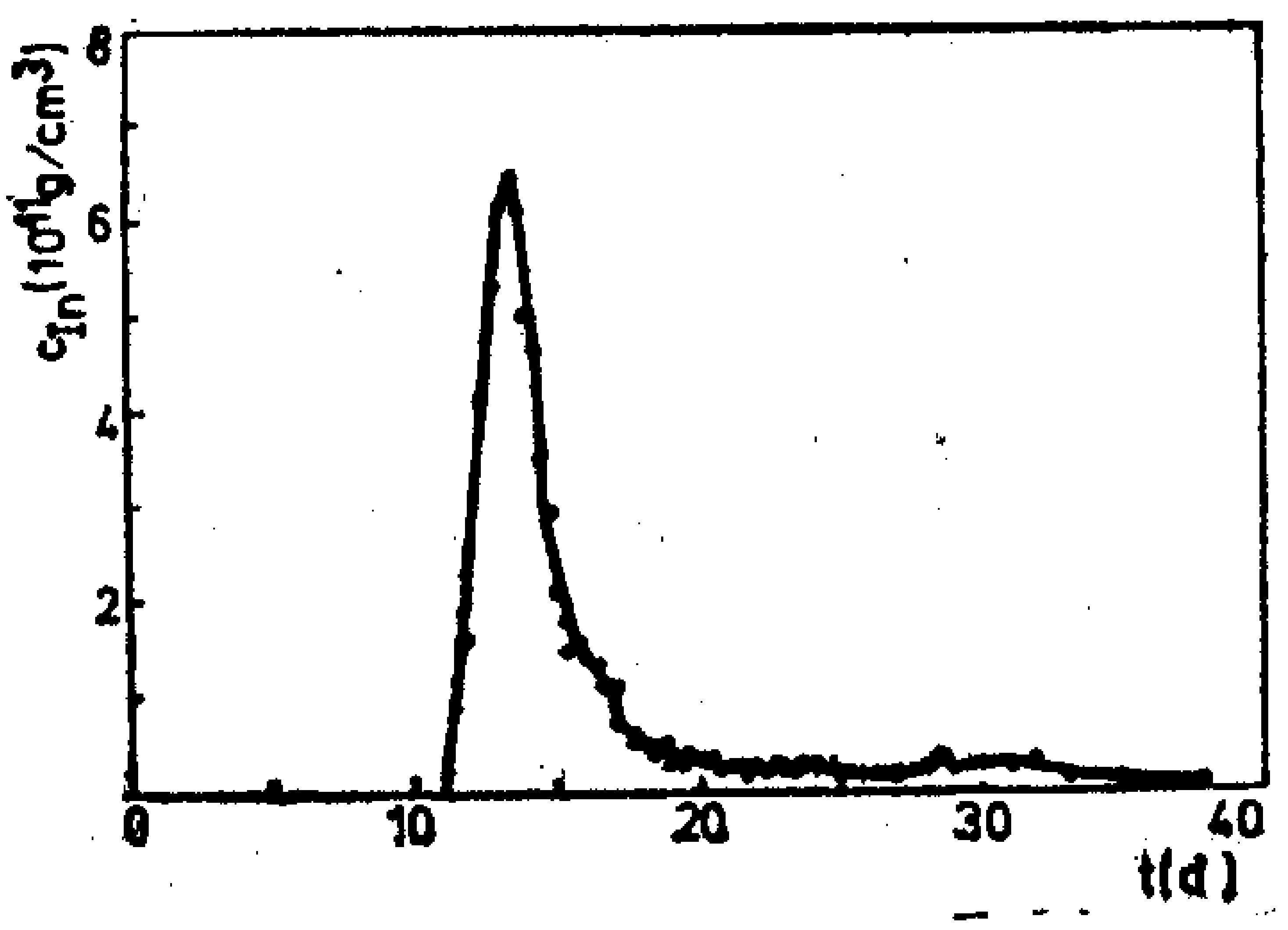

Fig. 3. Transfer curve obtained in Scorota sinkhole — Cerna spring experiment.

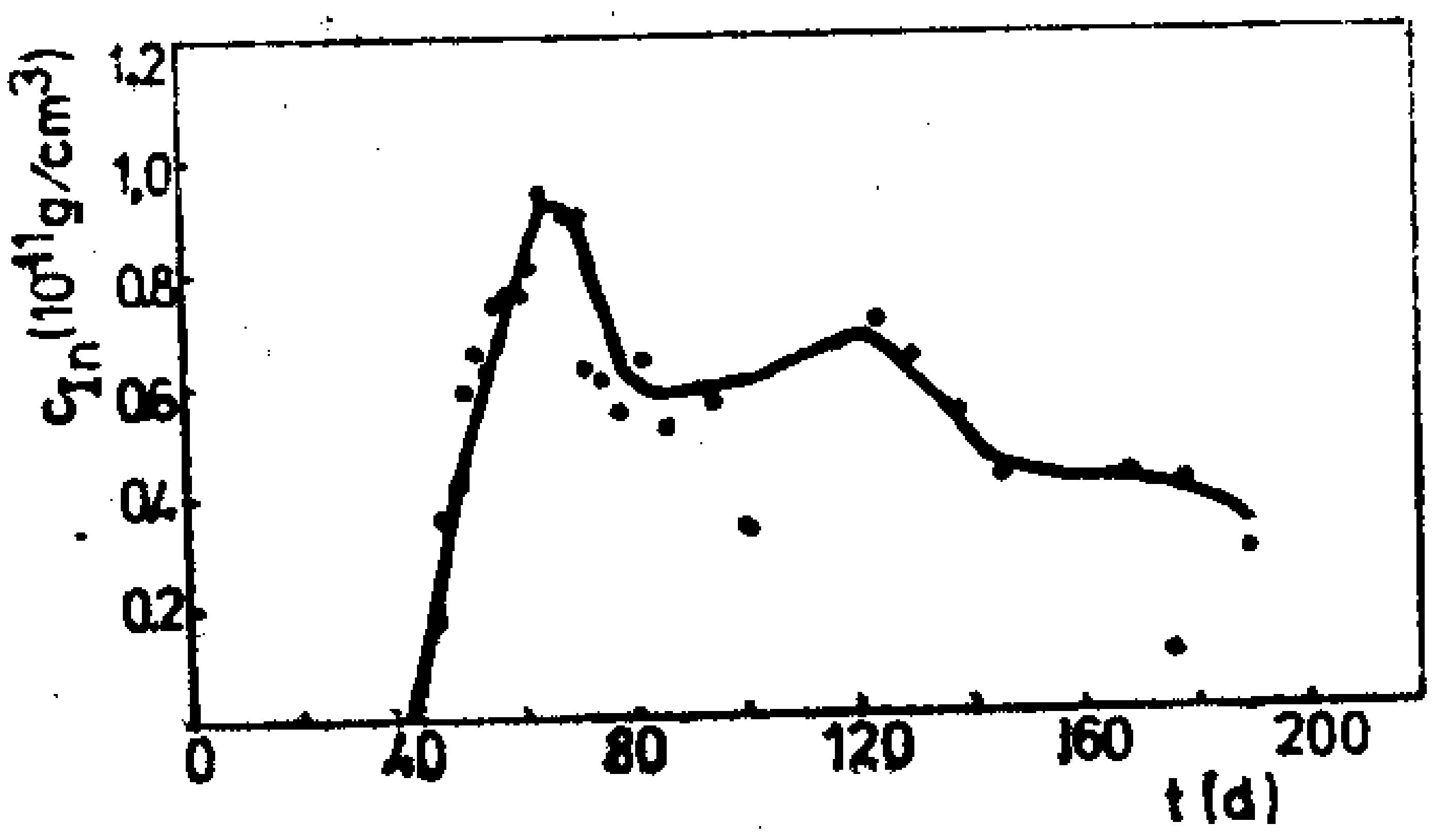

Fig. 4. A two-hundred days experiment with In-EDTA as a tracer: the tracer was injected in Bichii swallet and appeared after 40 days in Toplița de Vida spring.

ground path. Naturally, as the rains started to fall, the tracer retained in the sub-systems was carried along to the spring and even between these events, a trap might release all of its tracer load, for

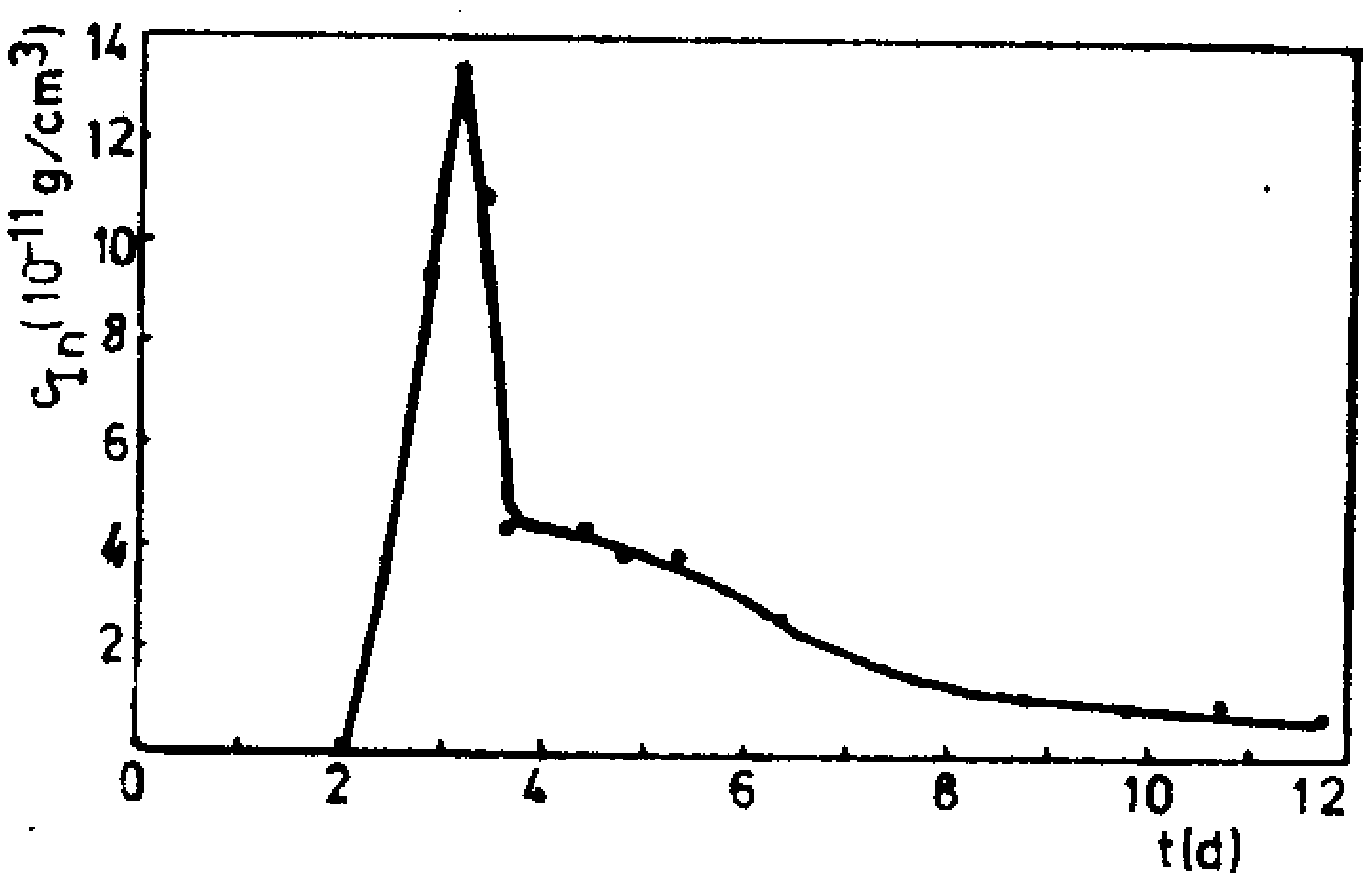

Fig. 5. A karstic difluence labelled with In-EDTA: Valea Luncilor—Izbucul Brătcanilor.

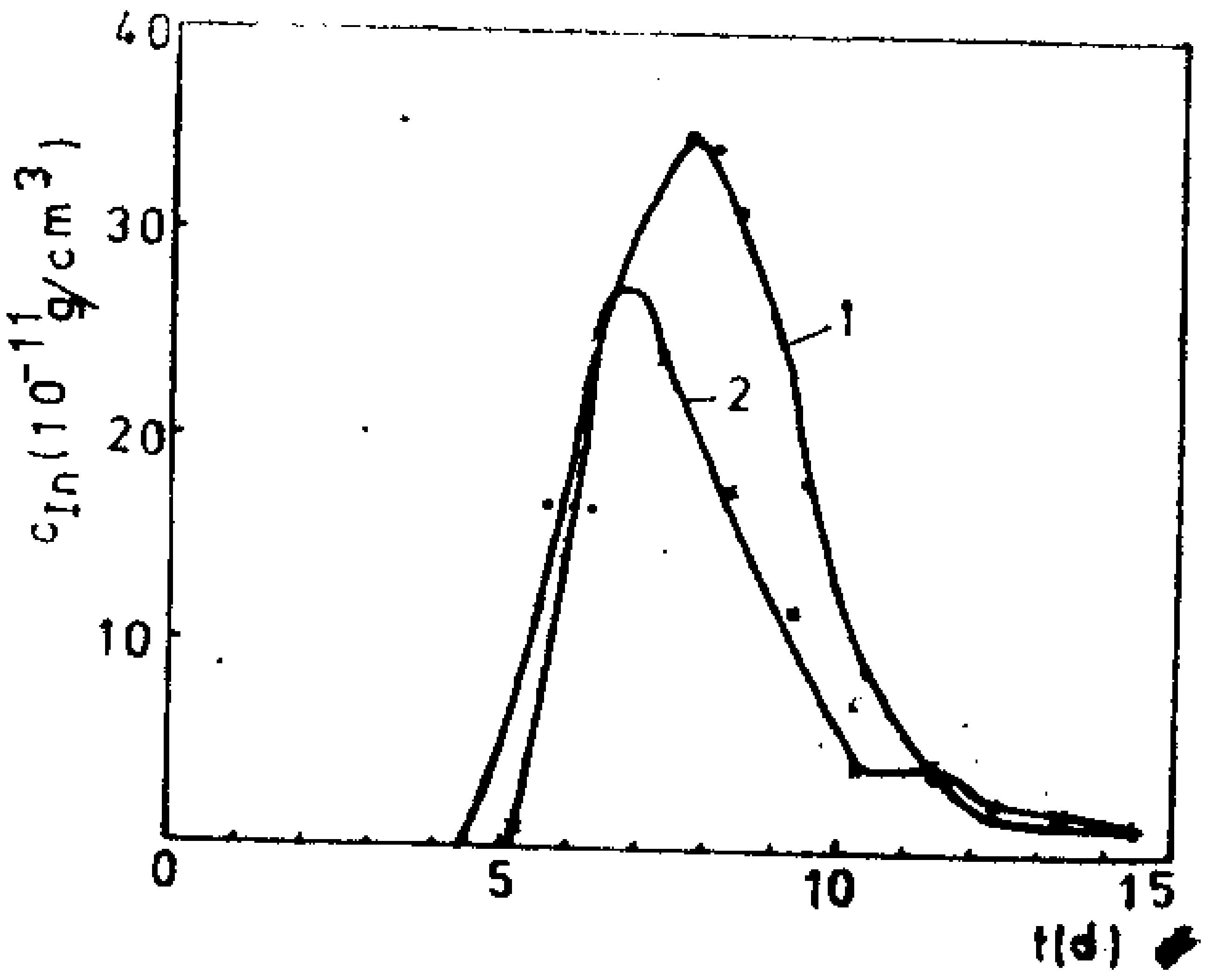

Fig. 6. Motru Sec experiment. The tracer was injected in a swallow-hole and appeared simultaneously in Bolboros spring (curve 1) and in Muncelu spring (curve 2).

local causes. and then a maximum like that shown in fig. 3 turns up in the measurements. Additionally, this labelling conducted in 1982 demonstrated the ability of indium as a tracer to label highest flowrates: the Cerna Spring flowrate during that period was of 2.7 m^3/s.

From the experimental labellings given in Table 1, a record of longevity stands out at least for the tracers employed in Romanian karsts. So, when the water of the Bichii swallet (in the Bihor District) were labelled with 10 g of In-EDTA, the tracer turned up 40 days later in the Toplița de Vida Spring (fig. 4). Then it was further measured for 155 days; the last measured sample was collected 206 days after labelling. The tracer amount recovered was of 64%. No other tracer would have survived for so long a time: the available radioactive tracers either decay or are retained by ionic exchange or other processes and the fluorescent tracers, are retained by the environment and are gradually decomposed by both water pollutants and oxidation in the aeration areas, in the sub-systems and in the free flow portions.

Such a long-time transit is in compliance with expectations. This is the ordinary behaviour of some karsts in the Bihor District during drought years. For instance, this is the case of tht Aştileu Spring: the waters of the Valea Pestişului swallow hole were In-labelled in June 4, 1983. The maximum In concentration turned up at the Aştileu water supply as late as 137 days after labelling.

5. CONCLUSIONS

Indium is at present the most appropriate tracer for water labelling in the karst structure of Romania.

As indium is ordinarily employed in extremely small amounts, it is anpolluting for all practical purposes, and may be used for labelling drinking water, as well as mineral and thermo-mineral waters in health resorts.

As tracer retention inside the karst is virtually insignificant, indium may be used for labelling waters of very long paths. Additionally, its special properties recommend it in labelling karst flow-rate in excess of 1 m^3/s : an artificial lake of 10 million m^3 can be labelled using 1 kg of In-EDTA.

The method used for tracer identification and measuring relieves in sensitivity and reproductibility, an improvement over methods emploved in other countries.

The costs of the tracer and measuring activities are comparable to those involved by radioactive tracers, but the working procedure is a bit more cumbersome.

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COMPORTAREA INDIULUI CA TRASOR PENTRU CERCETAREA APELOR CARSTICE

Rezumat

Introducerea utilizării indiului sub forma In-EDTA ca trasor activabil în cercetări hidrogeologice aduce o importantă contribuţie la studiul apelor carstice atît sub aspectul completării gamei de trasori utilizabili în astfel de studii cît şi prin avantajele pe care le are faţă de ceilalţi trasori.

Rezultatele obţinute în utilizarea indiului ca trasor în perioada 1982—1984 în diverse zone carstice din România concretizate printr-un număr de 15 marcări, au permis perfecţionarea metodei atît sub aspectul marcării (estimarea cantităţilor necesare pentru marcare), prelevării probelor cît şi al metodei de analiză prin activare cu neutroni.

S-au obţinut o serie de concluzii pozitive care recomandă utilizarea acestui trasor în mod special pentru cazurile în care ceilalţi trasori (radioactivi, fluorescenţi, chimici, etc.) au o aplicare limitată datorită degradării în timp, dezintegrării radioactive, radiotoxicităţii, interacţiilor cu mediul, etc.

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