# Comparative Investigations into Recent Methods of Tracing Subterranean Water

**By K. Buchtela, J. Mairhofer, V. Maurin, T. Papadimitropoulos, and J. Zötl**

## ABSTRACT

The growing number of investigations involving the tracing of subterranean water has led to the improvement of old methods of water tracing, such as the use of dyes and salts, and to the introduction of new methods, such as radioactive tracers, neutron activation analysis, and dyed lycopodium spores. Experiments comparing various methods of subterranean water tracing were conducted in the Buchkogel area near Graz, Austria, using Rhodamine B dye, ammonium bromide, radioactive iodine, and dyed lycopodium spores, during 1963.

Results of the experiments showed that lycopodium spores travel faster than other tracers. Bromine and Rhodamine B travel at approximately the same rates, whereas radioactive iodine moved more slowly than other tracers.

While each of the tracers proved successful, each has certain limitations. If the area of investigation is large, radioactive isotopes method is virtually ruled out because of the large number of personnel required, but the method should prove useful where the water is thought to flow through fine clastic sediments. Lycopodium spores would seem to be most useful for large areas, where several colors of dyed spores may be used to trace flow from several swallow holes simultaneously. However, the method is restricted to areas where flow is thought to be through open conduits. Rhodamine B has proven utility, but it is adsorbed by clays. A combined use of spores and Rhodamine B is of great utility. The neutron activation analysis method allows a fair estimate to be made of the water in the underground system, a feature that is not possible with other methods, but the amount of ammonium bromide required is appreciably larger than the amount of spores or dye.

## INTRODUCTION

Investigations into the distribution, flow direction, and flow rate of underground water have become increasingly important in the solution of problems of water supply, water power, and mining and tunneling. The growing number of such investigations has led to the improvement of old methods of water tracing and the introduction of new ones.

The older methods of water tracing that are still used include the addition of salts and dyes. The usual salt employed is NaCl and the resulting increase in $Cl^-$ in the water is determined by titration or electrical conductivity. In some instances the water being investigated has a high or variable $Cl^-$ content due to natural (*e.g.*, brackish water or saltwater springs) or artificial (*e.g.*, waste water) causes. In such cases LiCl or $(NH_4)_2SO_4$ have been used and determinations made for ions other than $Cl^-$. The numerous dyes which have been tested include eosine, fuchsin, Congo red, safranine, auramine, and uranine. Of these, the fluorescein salt uranine has proved to be the best. In extremely sour water (*e.g.*, in brown coal mines), acid fuchsin is used.

Soon after the discovery of radioactivity, radioactive material and radiation-recording equipment was applied to the problem of tracing underground waterways. Such investigative procedures using radioactive isotopes have been steadily improved. In the beginning, maximum permissible dosages of radiation were greatly exceeded because the dangers of radiation were not yet known.

Only recently has a method involving later activation (neutron activation analysis) been applied. The tracer, which is ammonium bromide ($HN_4Br$) in our case, is activated after collecting the samples. This has obvious advantages in that neither the half-life nor the radiation danger must be taken into account. For these reasons, this procedure and its future improvements deserve special attention. The method was developed by T. Papadimitropoulos and is treated in detail in this paper.

During the last few years, dyed lycopodium spores (*Lycopodium clavatum*) have been used with success in limestone and dolomite rocks (karst regions) where the subterranean water follows widened joints and clefts. This method is attractive because observation is simple and it is possible to conduct several tracing experiments simultaneously.

The tracing of bacteria has been used to solve special problems. This method requires much preparation and careful consideration.

Before deciding which method is to be used for the investigation of a specific area, several factors must be considered. If the area is large, the application of salt is almost ruled out. The transportation of large quantities of salt to a sinkhole, which may be situated in a relatively inaccessible area, as well as the observation of a large number of springs, presents tremendous difficulties. The use of dye is difficult if the water being investigated is turbid, and the calculation of the amount needed is often difficult. The considerable amount of necessary technical equipment limits the wide application of radioactive isotopes. Finally, the use of spores is not possible when fine clastic particles are present in the water. In many of our tests, therefore, it was necessary to use several methods simultaneously. This raised the question of how to compare data obtained by the various methods, and it was deemed necessary to test the different methods under the same conditions in a special experiment.

Such an experiment, combining the application of salt, dye, and spores, was successfully performed in 1956 by V. Maurin and J. Zötl in the Buchkogel area in the outskirts of Graz, Austria. The subterranean drainage system in this area had been investigated previously by hydrogeologic mapping and experiments. A comparative experiment was conducted in the same area in July of 1963 using Rhodamine B, radioactive isotopes ($I^{131}$ and $Rb^{86}$), ammonium bromide, and lycopodium powder dyed various colors. This last experiment, which is the subject of this paper, had as its purposes the comparison of modern investigative methods and the aquisition of experience with some of the newer techniques.

The experiment was subsidized by the Vereinigung für hydrogeologische Forschungengen in Graz and was organized by its representatives Dozent Dr. V. Maurin and Dozent Dr. J. Zötl. The following acted as Cooperators:

Dr. K. Buchtela, Atominstitut der Osterreichischen Hochschulen, Vienna.

Dr. J. Mairhofer, Bundesversuch- and Forschungsanstalt Arsenal, Vienna, in cooperation with M. Borowczyk, civ. eng., and A. Zuber, civ. eng., Poland.

Dozent Dr. V. Maurin, Institut für Mineralogie and Technische Geologie an der Technischen Hochschule, Graz.

T. Papadimitropoulos, Nuclear Research Center "Democritus," Athens.

Dozent, Dr. J. Zötl, Geographisches Institut der Universitat, Graz, Graz.

Altogether, a total of 23 persons took an active part in the work connected with the introductions of material and observations carried out during the six-day experiment.

Grateful acknowledgement is due our cooperators who performed the neutron activation and analyses at the Nuclear Research Center "Democritus" and in the Austrian Nuclear Research Institute.

## THE AREA INVESTIGATED AND ITS DRAINAGE

Graz, the capital of the Austrian province of Styria, is situated in the northern part of the Pleistocene terraces of the Grazer Feld.

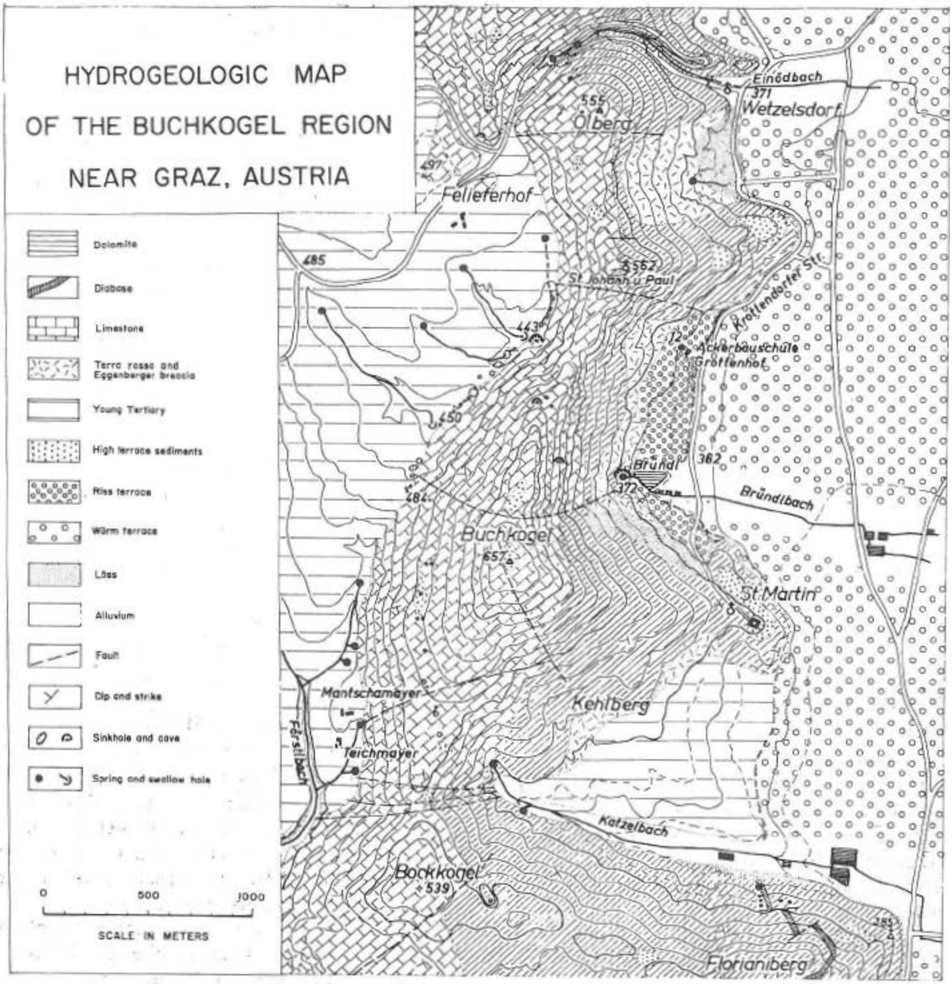

Figure 1.
Map of the area investigated near Graz, Austria. The swallow hole is at point 443; Bründl Spring is at point 372.

The Buchkogel mountain range forms the western boundary of and lies about 300 meters (1000 feet) above the open and relatively level Grazer Feld. This 9 kilometer (5.6 mile) long north-trending range (fig. 1) is considered to be an outlying range of the Alps. It is underlain by limestones and dolomites of Devonian age which dip moderately steeply beneath the Tertiary sediments of the Styrian Basin to the east. The rocks of the Buchkogel range are broken by several east-west faults which have influenced the hydrology. Karst topography is developed on both the limestones and dolomites.

The Buchkogel range was completely buried during the early Tertiary. It was exhumed by regional uplift during the late Pliocene. The Tertiary clays, sands, and gravels east of the range are covered by Pleistocene gravels. In the area of Tertiary outcrop west of the range are several small streams which disappear into sinkholes at the foot of the Buchkogel range, thus draining completely underground an area of 1.4 square kilometers (0.54 square mile).

It was long assumed that the water which disappeared west of the range probably emerged at the Bründl spring at the east foot of the range. This spring rises 71 meters below the lowest swallow hole and 800 meters distant.

Furthermore, a chemical examination of all of the springs on the east, south, and southwest sides of the Buchkogel range indicated that the water which goes underground in the swallow holes emerges at the Bründl spring. This was confirmed by a salt-tracing experiment conducted May 12-14, 1956 (Maurin and Zötl, 1959, p. 16 and following).

Because the hydrogeology was so well known, the area was chosen for further experiments. After improving the practicability of spore tracing by dyeing the spores, a combined experiment using salt, dye, and spores was undertaken on June 22-28 in order to compare these methods (Maurin and Zötl, 1959, p. 21 and following). The success of this experiment encouraged us to undertake another comparative experiment in the same area. This paper describes the results of this last experiment, which was carried out during July 1963.

The injection of labeled material (Rhodamine B, ammonium bromide, dyed Lycopodium spores, and radioactive isotopes) took place July 1, 1963, from 1400 h to 1800 h.

Due to several weeks of dry weather preceeding the introduction of labeled material, the small streams west of the Buchkogel range were nearly dry, and the rate of inflow into the swallow hole (fig. 1, point 443) was only 0.58 liter/sec. The discharge of the Bründl spring was also quite low: 7.5 liters/sec at the beginning of the experiment. Following a rainfall that started at 1400 h on July 2, the srping discharge rose to 14.9 liters/sec at 1900 h. This additional flow was derived mainly from the vicinity of the spring. By 2200 h the discharge had declined to 11.4 liters/sec. Infiltration from the higher parts of the range and the Teritary area to the west was not apparent until July 3, when the discharge rose to 15 liters/sec at 0200 h. During July 3, the discharge of the spring declined to 8.4 liters/sec and remained at about this value throughout the remainder of the observation period (fig. 17).

The water temperature at the Bründl spring varied only from 9.8° to 10.0°C during the period of the experiment, in spite of the considerable variations in discharge.

## THE SPORE METHOD

The spores of *Lycopodium clavatum* have been successfully used in hydrologic experiments in several Alpine karst regions (Zötl, 1961). Lycopodium spores have a diameter of about 35$\mu$ and tend to remain suspended in moving water. They are thus able to pass through siphons which trap floating particles. The spores are caught at a resurgence with a plankton net (fig. 2). Because the net is in position continuously, it is sufficient to collect only one sample per day to determine the quantity of spores. One person is thus able to inspect a number of resurgences. An exact description of the method will be found in Maurin and Zötl (1959).

Spores cannot be used in areas of sand and gravel because they tend to be filtered out. In extensive limestone and dolomite areas, however, this method has proved successful.

The experiment reported here served several purposes. In addition to providing data

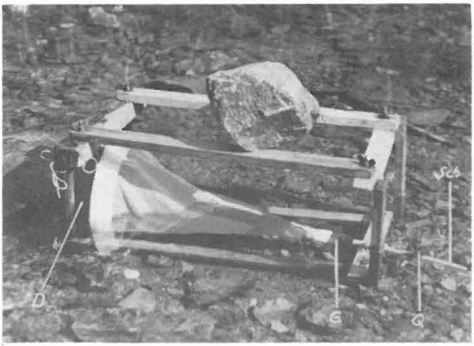

Figure 2.
Plankton net in the Bründl Spring, showing the wooden frame used to support the net. D, wire mesh covering the front opening to exclude coarse material; G, glass funnel attached to net; Sch, rubber tubing; Q, pinch clamp.

for comparison with other methods, a new color of dye was introduced and nets of different sizes and fabrics were tested.

Two kilograms of *Lycopodium* powder dyed brown (the new color) were injected on July 1, 1963 from 1545 to 1555 h, and three kilograms of powder dyed blue (a color we have been using from the beginning) were injected from 1600 to 1610 h into the swallowhole near Felieferhof (fig. 1, point 443). As is the habit in precise experiments the plankton nets were installed at the same time. Samples were taken hourly from July 1, 1963 at 1800 h to July 6 at 1550 h.

The first spores appeared in the sample collected at 0100 h on July 3, and the first peak was reached in the sample collected at 0700 h on July 3 (this sample, which was collected from the standard net, contained 124 brown and 202 blue spores for a total of 326). The quantity of spores in the samples then dropped suddenly and the samples collected on July 3 at 1100, 1300, and from 1500 to 1700 h contained no spores at all.

Another wave of spores began at 1800 h and reached a second peak on July 3 from

Figure 3.
Scene at the swallow hole showing the barrel used to dilute the ammonium bromide and the funnel for introducing spores. Entrance to Felieferhof cave in background, through which stream flows for a short distance.

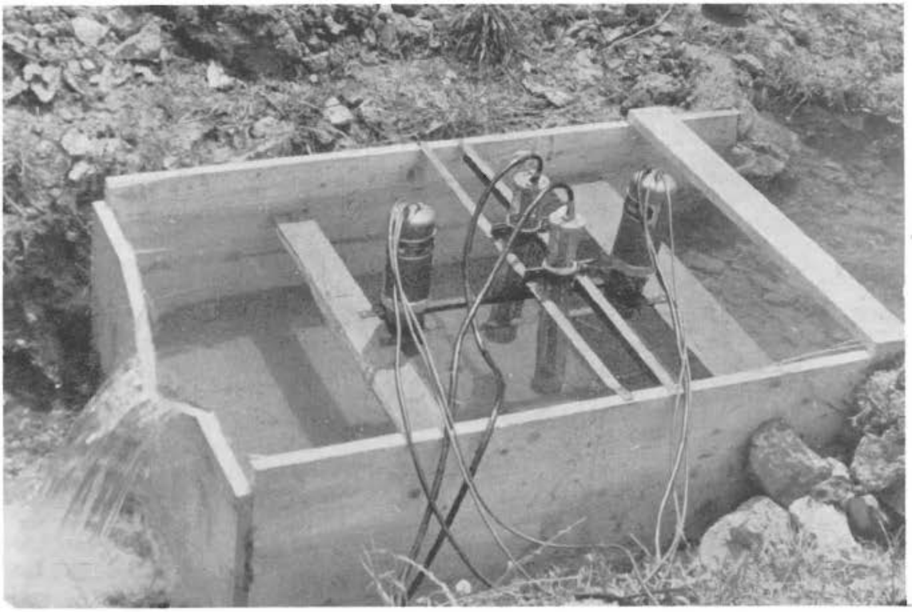

Figure 4.
Radiation detectors and measuring box at Bründl Spring.

2000 h (52 hours after injection) to 2200 h (2000 h: 75 brown, 106 blue, 181 total; 2100 h: 65 brown, 98 blue, 163 total: 220 h: 96 brown, 190 blue, 286 total). The number of spores then decreased fairly rapidly to 0400 h on July 4, and only occasional later samples contained a few spores. After 1900 h on July 5 all samples were free of spores.

A total of 440 brown and 696 blue spores were collected at Bründl spring. The ratio of the two colors was in approximate accordance with the 2:3 ratio of the amounts injected.

## THE DYE METHOD

In earlier comparison experiments we had used the dye Uranine AP conc. (made by E. Merck in Darmstadt, Germany) together with other labeled material. Rhodamine B, a dye which had been used several times in other countries, was used in the present experiment. One and one-half kilograms of dye was diluted in an 80 liter barrel of water and introduced into the swallow hole southeast of Felieferhof (fig. 1, point 443) from 1450 to 1510 h on July 1, 1963. The amount used, which was rather large for this small karst system, was about the same as the amount of Uranine which was used in the 1956 experiment. This offered further possibilities for comparison.

Samples were collected from the Bründl spring beginning at 1800 h on July 1. The first trace of dye was in the sample collected at 0900 h on July 3, 42 hours after introduction. The dye was detected in this sample by means of an ultra-violet lamp and the concentration was about $10^{-9}$. Two hours later, at 1100 h, a slight coloration could be detected with the naked eye, and an intense red color had developed in the water by 1300 h. The peak of the coloration (concentration about $10^{-6}$) was in the sample collected at 1200 h on July 4, 69 hours after introduction (see fig. 17). The dye concentration then decreased slowly to 1200 h on July 7 and slight traces were apparent until July 14. After July 7 only two samples were collected daily.

About the same peak concentration was reached as in the 1956 experiment with Uranine. A striking difference between the two experiments was that the Rhodamine was adsorbed on and colored organic material and clays. This was well illustrated by the plankton nets. The silk nets developed a distinct red color while the synthetic fiber net was unaffected. The dye was largely washed off the silk net after several days. This adsorption and slow washing-off process explains why the dye was present in the Bründl spring for such a long time.

## THE RADIOACTIVE ISOTOPES METHOD

(J. Mairhofer)

For this experiment the Isotope Department of the Austrian Federal Testing and Research Institute Arsenal selected the radioactive nuclides I-131 and Rb-86 in order to compare their effectiveness in determining the flow velocities of karst groundwater. Earlier studies have shown that both of these nuclides are only slightly adsorbed. The energies of I-131 (0.36 million electron volts) and Rb-86 (1.078 mev) can be precisely separated and two one-channel analyzers (scintillation counters) were used for the separate determination of the two nuclides. In addition, a Geiger-Müller beta counter (Philips 19553) to determine I-131 plus Rb-86. The experiment included both (a) measurement of water flow rate and (b) measurement of the total amount of subsurface water by means of the Total Count Method described below. The detectors were equipped with scalers and multipliers as well as recorders.

The relationship of the various injection and measuring points is shown schematically in figure 5. In order to determine the flow volume above the swallow hole, I-131 was introduced at point $I_1$ and measured with two Geiger-Müller tubes in parallel at point $M_1$, a short distance above the swallowhole. Because the flow was small, it was also measured directly.

Forty-five minutes after the above injection, both I-131 and Rb-86 were introduced into the swallow hole just downstream from point $M_1$. Two scintillation counters and paralleled Geiger-Müller tubes (fig. 4) were installed at point $M_2$, a short distance downstream from the resurgence (point $I_3$). Finally, I-131 was introduced at point $I_3$ to determine the flow from the spring. The flow volume was also determined by direct measurement.

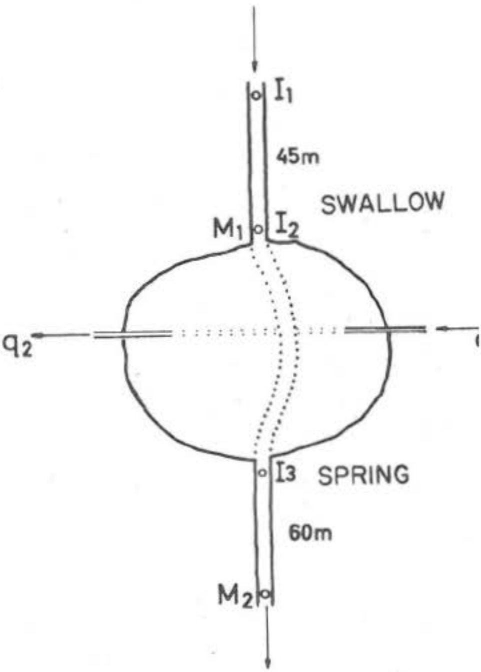

Figure 5.
Diagrammatic representation of under ground water system. See text for explanation.

### DETERMINATION OF FLOW TIME

Three hundred millicuries of I-131 as Na was introduced at 1715 h and 100 mC o Rb-86 as RbCl was introduced at 1800 h on July 1, 1963 into the swallow hole. The first trace of activity at point $I_2$ appeared a approximately 1300 h on July 3. Activity increased to a peak at about 1300 h on July 5 and then declined (fig. 6), giving a transit time of 78 hours. The activity had not yet returned to zero by 1500 h on July 6.

Unfortunately, the Rb-86 analyzer was inoperative during the experiment. Because both the I-131 scintillation counter and the Geiger-Muller tubes peaked at about the same time, it is concluded that the Rb-86 was either strongly adsorbed or swamped out by the I-131 radiation. Figure 6 also shows the flowrate at point $M_2$ as measured by a Thompson overflow wier.

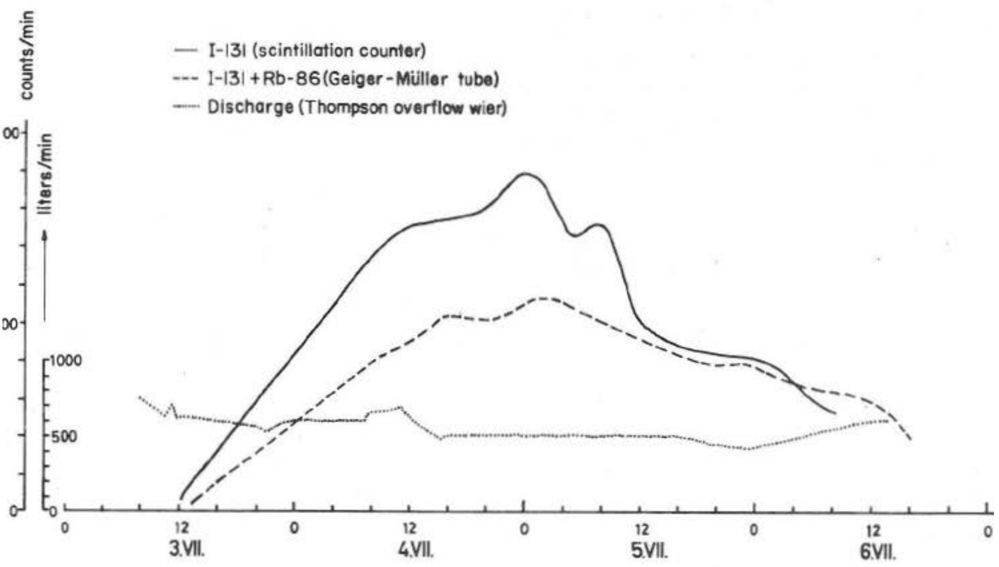

Figure 6.
Plots of activity and discharge at Bründl Spring.

*Determination of total subsurface water volume by the Total Count Method*

The Total Count Method is based on the relationship that the water volume is directly proportional to the applied activity and inversely proportional to the total count, or

$$Q = F \cdot A / N$$

where Q is the water volume in liters per minute, A is the activity in millicuries, N is the total counts recorded, and F is a proportionality constant which depends on the detectors and the counting geometry.

The calibration factor F was determined for point $M_1$ with the small measuring box as

$$F = 7.3 \times 10^3 \text{ liter-counts/mC-min}$$

Thirteen mC of I-131 were injected at point $I_1$ and 3 to 4 minutes later a clear peak was recorded at point $M_1$. The magnitude of the peak yielded a value for the flow of 38.2 l/min ($= Q_1$), which was in good agreement with a wier measurement at $M_1$ of 34.6 l/min.

A value of F for the larger measuring box at point $M_2$ was determined for I-131 and Rb-86 as well as for the two together. Using this value for F, the flow at $M_2$ ($= Q_3$) was determined by injecting 10 mC of I-131 at point $I_3$. The value obtained was 390 l/min, as compared to 470 l/min based on the Thompson overflow wier.

Because of the lack of agreement between the two values of $Q_3$, tests were conducted in the laboratory subsequent to the field experiment. The geometrical conditions of these tests were the same as those at point $M_1$, and the results are shown in figures 7 and 8. The calibration factor determined in the laboratory was slightly higher than that used in the field. Based on this new value of F, $Q_3$ = 700 l/min. This is higher than the value determined by direct flow measurements. It is apparent that the exact value of F is both difficult to determine and of great influence on the final flow determination.

Although I-131 and Rb-86 radiate different energies, the calibration factor for the two nuclides is nearly the same, as shown in figure 7. The dashed part of the Rb-86 curve in this figure is probably due to contamination from an earlier test with I-131 and hence spurious.

The counting response is very sensitive to the immersion depth of the probe (fig. 8). This may account for at least part of

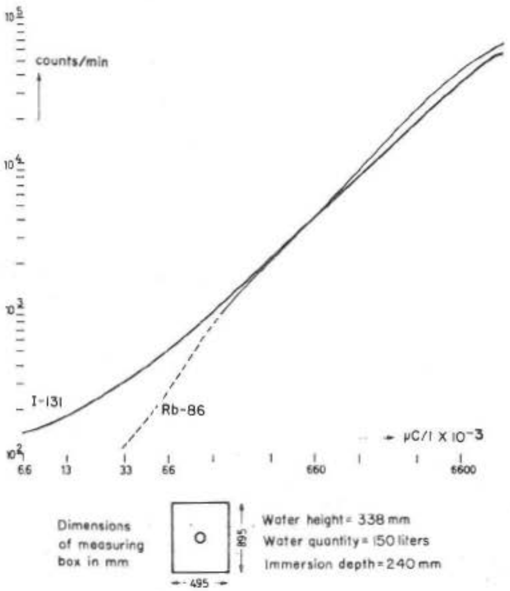

Figure 7.
Results of adjustment test. See text for explanation.

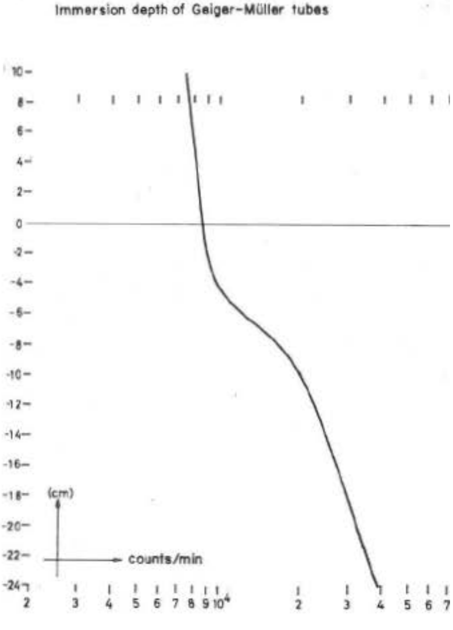

Figure 8.
Results of adjustment test (immersion depth). See text.

the flowrate discrepancy. The high counting rate above the water is due to relatively large amount (2 mC) of Rb-86 used in the test.

Based on a comparison of the counting rate at point $M_2$ and the amount of radioactive material introduced at point $I_2$, it can be shown that the flow from the swallow hole is augmented by other water before it reaches the spring. Based on the field value F, the maximum flow between the swallow hole and the spring is 690 l/min ($Q_2$). The added flow, designated $q_1$ ($= Q_2 - Q_1$) is equal to 650 l/min. Part of $Q_2$, however, is diverted and does not emerge at the spring. This diverted flow, $q_2$, ($= Q_2 - Q_3$), amounts to 300 l/min. Thus the Bründl spring is not the sole discharge from the subsurface karst system.

If it is assumed that all of the radioactive material had been discharged through the spring in the 80 hours after the injection, the volume of the reservoir between the swallow hole and the spring is 3310 cubic meters.

## THE NEUTRON ACTIVATION ANALYSIS METHOD, PART I

(T. Papadimitropoulos)

The neutron activation analysis method fo tracing underground water involves the introduction of a non-radioactive nuclide int a swallow hole and the collection of sample at springs, the irradiation of the sample with neutrons, and the detection of the radioactive nuclide thus produced. The metho had been used in a study in Greece (Dimitroulas, *et al.,* 1962) prior to the presen experiment.

Ammonium bromide, a cheap and easil available compound, was used in the experiment. The nuclide Br-81 has a natural abundance of 50% and a cross section of 3. barns. The radioactive nuclide produced b neutron activation, Br-82, has a half life o 35.9 hours.

This study was undertaken at the reques of the Vereinigung für hydrogeologische Forschungen in Graz so as to demonstrate th method to a group of hydrogeologists studying different methods of water tracing and

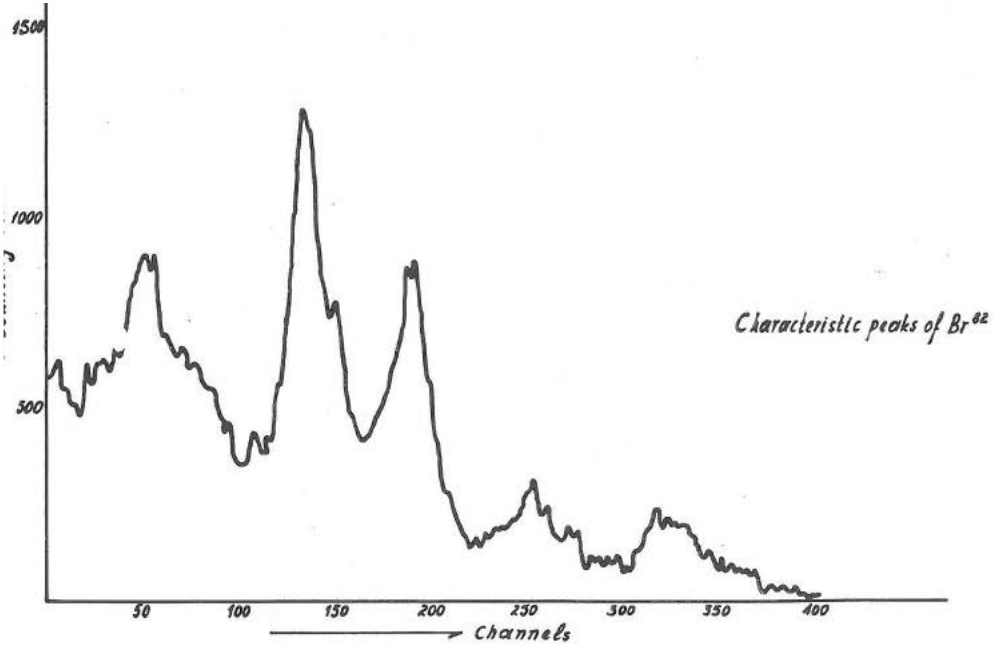

Figure 9.
Energy spectrum of sample 69. See text.

to compare the data obtained with that derived from other methods of investigation. Activation and analyses of samples were performed both at the Nuclear Research Center "Democritos" in Athens and at the Atominstitut der "Österreichischen Hochschulen in Vienna. This section describes the results of the investigation done in Athens. The results of the Vienna work are discussed in the following section.

From 1515 h to 1538 h on July 1, 1963, 30 kg of $NH_4Br$ dissolved in 120 liters of water was introduced into the swallow hole southeast of Felieferhof. Starting at 1800 h on 1 July, 100 ml samples were collected at the Bründl spring at 30 minute intervals (one liter samples were also collected hourly for the Vienna determinations). After 2000 hours on July 6 only two samples a day were collected through July 7.

Before starting the experiment, the water of the Bründl spring was analyzed for its bromine content. The amount of natural bromine was found to be negligible (about 0.05 mg/1). Ten liters of the uncontaminated spring water were also collected for later use.

Following the experiment, the samples were taken to Athens, where each was filtered to remove any soil contamination. A 5 ml fraction of each sample was placed in a polyethylene vial and irradiated in the reactor core with a neutron flux on the order of $10^{10}$ to $10^{11}$ neutrons/cm.$^2$ sec. Five ml fractions of the uncontaminated spring water were also irradiated with the same flux. Qualitative analysis of each of the samples was done using a well-type of scintillation counter (Nuclear Chicago model DC-5) with an electronic circuit designed by the Electronics Department of the N.R.C. "Democritus". The gamma-ray spectroscopy was performed with a 400 channel analyzer of the Intertechnique S.A. France.

Of the 206 samples analyzed, Br-82 activity was found in 76. These were samples number 38, collected at 0900 h on July 3, to number 113a, collected at 2030 h on July 6. The spectra of these samples contain all the characteristic peaks on Br-82, which are well known. A typical spectrum of a sample (number 69) close to the concentration maximum is shown in figure 9.

Each of the 76 samples in which bromine

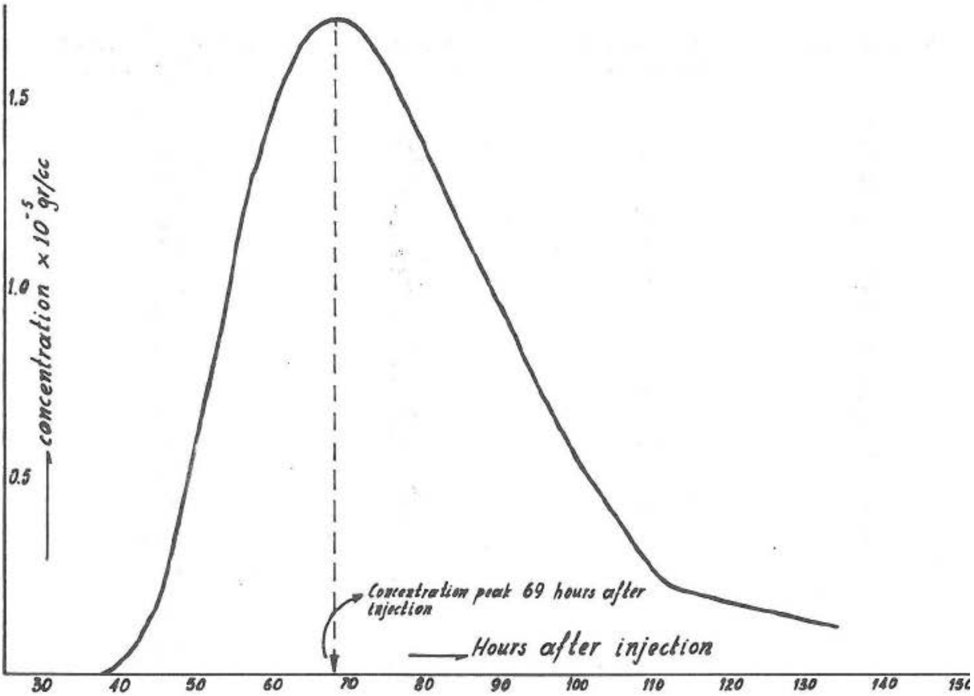

Figure 10.
Concentration versus time curve. See text.

was detected was then analyzed quantitatively for bromine by irradiating a sample fraction together with a standard consisting of a 10 mg/1 solution of $NH_4Br$ made up using the uncontaminated spring water.

The first trace of $NH_4Br$ was observed at the spring 41.5 hours after its introduction into the swallow hole (figure 10). Maximum concentration occurred 26.5 hours later (68.0 hours after introduction). After about 75 hours from the first appearance (117 hours after introduction) the concentration had decreased to the limits of detectability.

The discharge rate of the spring and its variation with time during the experiment are shown in figure 11. From these values the average discharge rate has been computed to be 8.795 1/sec ($=3.17 \times 10^7$ $cm^3/hr$). The volume of water discharged during the 75.5 hours during which the water was sampled (after the bromine appeared) is $2.4 \times 10^9$ $cm^3$. The average concentration of ammonium bromide calculated from the data of Table 1 is about $0.93 \times 10^{-5}$ $g/cm^3$. The quantity of $NH_4Br$ which emerged from the spring is therefore $2.9 \times 10^9$ $cm^3 \times 0.93 \times 10^{-5}$ $g/cm^3$ or 22.3 kg.

This amount is 76% of the 30 kg introduced into the swallow hole. The 24% not accounted for may have left the spring in concentrations too low to be detected, or may have remained in the underground water body.

Denoting the amount of tracer added to the system by m and the concentration at time t by c, the flow rate F at any point in the system is $F = \int_0^\infty m/c\ dt$. The volume of water V, underground between the swallow hole and the spring is equal to the product of the flowrate and the average residence time T, given by $T = \int_0^\infty c\ t\ dt \,/ \int_0^\infty c\ dt$. Thus $V = F \int_0^\infty c\,t\,dt / \int_0^\infty c\,dt$.

These integrals may be computed from the areas under the curves of figures 10 and 12. Substituting the measured values of c and ct from table 1, the volume of water

## TABLE 1

| No. of sample | Time after injection in hours | Concentration $\times 10^{-5}$ gr/cc | Concentration x time $\times 10^{-5}$ gr/cc x h |
|---|---|---|---|
| 38 | 41.5 | 0.060 | 2.49 |
| 39 | 42.5 | 0.088 | 3.74 |
| 40 | 43.5 | 0.097 | 4.22 |
| 41 | 44.5 | 0.149 | 6.63 |
| 42 | 45.5 | 0.205 | 9.33 |
| 43a | 47.- | 0.360 | 16.92 |
| 44a | 48.- | 0.420 | 20.16 |
| 45a | 49.- | .0490 | 24.01 |
| 46a | 50.- | 0.620 | 31.00 |
| 47a | 51.- | 0.650 | 33.15 |
| 48a | 52.- | 0.750 | 39.00 |
| 49a | 53.- | 1.000 | 53.00 |
| 50a | 54.- | 1.050 | 56.70 |
| 51a | 55.- | 0.820 | 45.10 |
| 52a | 56.- | 0.890 | 49.84 |
| 53a | 57.- | 1.270 | 72.39 |
| 54a | 58.- | 1.330 | 77.14 |
| 55a | 59.- | 1.120 | 66.08 |
| 56a | 60.- | 1.150 | 69.00 |
| 57a | 61.- | 1.460 | 89.06 |
| 58a | 62.- | 1.440 | 89.28 |
| 59a | 63.- | 1.510 | 95.13 |
| 60a | 64.- | 1.570 | 100.48 |
| 61a | 65.- | 1.680 | 109.20 |
| 62a | 66.- | 1,720 | 113.52 |
| 63a | 67.- | 1.690 | 113.23 |
| 64a | 68.- | 1.730 | 117.64 |
| 65a | 69.- | 1.720 | 118.68 |
| 66a | 70.- | 1.700 | 119.00 |
| 67a | 71.- | 1.670 | 118.57 |
| 68a | 72.- | 1.690 | 121.68 |
| 69a | 73.- | 1.650 | 120.45 |
| 70a | 74.- | 1.700 | 125.80 |
| 71a | 75.- | 1.630 | 122.25 |
| 72a | 76.- | 1.670 | 126.92 |
| 73a | 77.- | 1.530 | 117.81 |
| 74a | 78.- | 1.570 | 122.46 |
| 75a | 79.- | 1.510 | 119.29 |
| 76a | 80.- | 1.500 | 120.00 |
| 77a | 81.- | 1.320 | 106.92 |
| 78a | 82.- | 1.360 | 111.52 |
| 79a | 83.- | 1.270 | 105.41 |
| 80a | 84.- | 1.260 | 105.84 |
| 81a | 85.- | 1.150 | 97.75 |
| 82a | 86.- | 1.130 | 97-18 |
| 83a | 87.- | 1.150 | 100.05 |
| 84a | 88.- | 1.120 | 98.56 |
| 85a | 89.- | 1.070 | 95.23 |
| 86a | 80.- | 1.080 | 97.20 |
| 87a | 91.- | 0.880 | 80.08 |
| 88a | 92.- | 0.840 | 77.28 |
| 89a | 93.- | 1.020 | 94.86 |
| 90a | 94.- | 1.000 | 94.00 |
| 91a | 95.- | 0.670 | 63.65 |
| 92a | 96.- | 0.640 | 61.44 |
| 93a | 97.- | 0.709 | 68.77 |
| 94a | 98.- | 0.697 | 68.30 |
| 95a | 99.- | 0.691 | 68.41 |
| 96a | 100.- | 0.608 | 60.80 |
| 97a | 101.- | 0.606 | 61.21 |
| 98a | 102.- | 0.583 | 59.47 |
| 99a | 103.- | 0.543 | 55.93 |
| 100a | 104.- | 0.472 | 42.09 |
| 101a | 105.- | 0.439 | 46.09 |
| 102a | 106.- | 0.405 | 42.93 |
| 103a | 107.- | 0.397 | 42.48 |
| 104a | 108.- | 0.359 | 38.77 |
| 105a | 109.- | 0.329 | 35.86 |
| 106a | 110.- | 0.274 | 30.14 |
| 107a | 111.- | 0.235 | 26.08 |
| 108a | 112.- | 0.231 | 25.87 |
| 109a | 113.- | 0.220 | 24.86 |
| 110a | 114.- | 0.220 | 25.08 |
| 111a | 115.- | 0.208 | 23.92 |
| 112a | 116.- | 0.205 | 23.78 |
| 113a | 117.- | 0.200 | 23.40 |

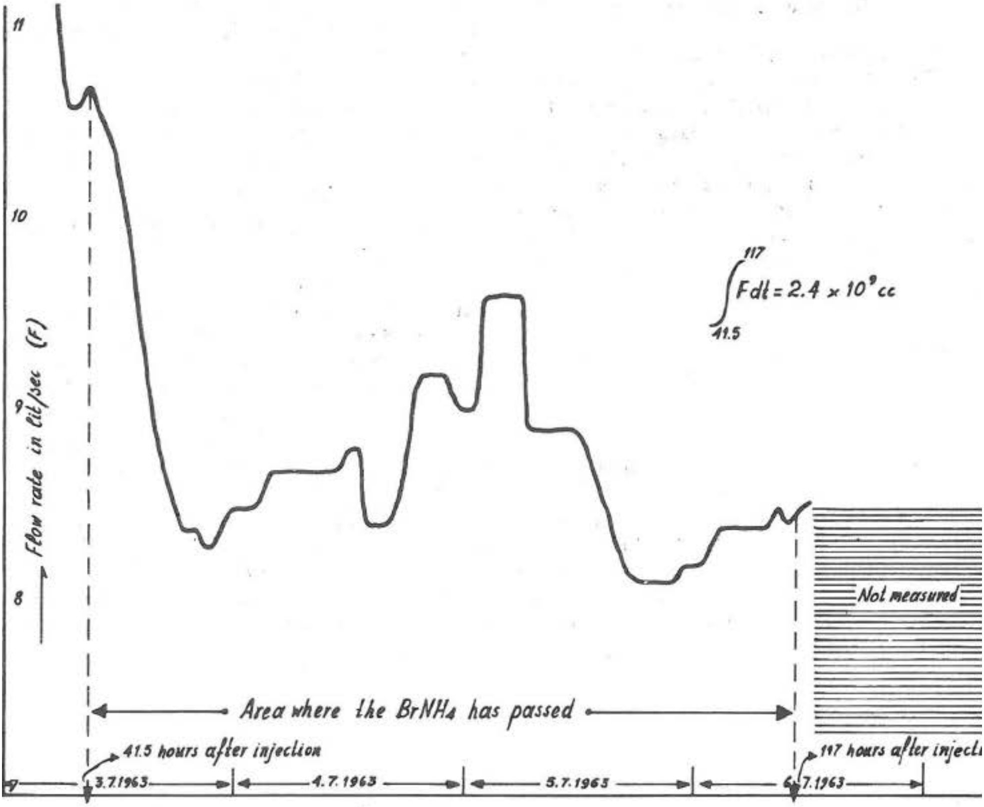

Figure 11.
Flow-rate versus time curve. See text.

between the swallow hole and the spring is found to be 2240 m³. This value represents a lower limit, inasmuch as only 76% of the tracer was accounted for.

## THE NEUTRON ACTIVATION ANALYSIS METHOD, PART II

(K. Buchtela)

Natural bromine consists of approximately equal amounts of Br-79 and Br-81. When these nuclides are irradiated with thermal neutrons, the nuclides Br-80, Br-82, and the isomer nuclide Br-80m are produced. The properties of these radionuclides are given in table 2.

Qualitative or quantitative analyses for bromine can be performed by measuring the radioactivity of the nuclide produced by irradiating the sample with thermal neutrons. By employing separation procedures (which are often tedious and time consuming), as little as $10^{-9}$ g of bromine can be determined.

**TABLE 2**

| nuclide | half life | radiation energy (mev) | daughter |
|---|---|---|---|
| Br-80m | 4.4 hrs | 0.04; 0.05 | Br-80 |
| Br-80 | 17.7 min | 2.0 ; 1.4 | Kr-80 (stable) |
| | | 0.86 | |
| | | 0.62 | |
| Br-82 | 35.9 hrs | 0.46 | Kr-82 (stable) |
| | | 0.55; 0.78 | |

### IRRADIATION OF SAMPLES

The activation analysis was performed at the TRIGA reactor of the Atominstitut der osterreichischen Hochschulen. The project involved the analysis of a large number of water samples, and it was necessary that as little as $10^{-7}$ g of bromine be detected. Table 3 shows the radioactivity of a 1 $\mu$g sample of bromine after irradiation for 50 minutes in a neutron flux of $0.7 \times 10^{12}$ neutrons/cm$^2$-sec.

**TABLE 3**

| radionuclide | microcuries per microgram |
|---|---|
| Br-80m | 0.026 |
| Br-80 | 0.53 |
| Br-82 | 0.04 |

After irradiation, the water samples contain not only radioactive bromine but also radioactive nuclides which were produced from other elements in solution in the water sample. It is necessary, therefore, that either the bromine be separated and purified or that the gamma-ray intensity at a selected wavelength be measured with a single-channel analyzer. Bromine-80 has a characteristic gamma peak at 0.62 mev. As shown in Table 3, high disintegration rates are obtainable even after only a short irradiation time. After an irradiation time of 50 minutes, most of the activity is due to Br-80.

### MEASUREMENT OF THE SAMPLES

After irradiation, the activity corresponds to the equation

$$A_t = A_o\ e^{-\lambda t}$$

where $A_t$ is the activity at time t, $A_o$ the activity at time 0, and $\lambda$ is the decay constant. Many radioactive nuclides decay to a radioactive daughter nuclide (*e.g.,* Br-80, see Table 2). This type of decay cannot be calculated by the above equation. Figure 13 is a plot of radioactivity versus time since irradiation for a bromine sample (mixture of Br-80, Br-80m, and Br-82, measured at 0.62 mev, time of irradiation: 50 minutes, flux: $0.7 \times 10^{12}$ neutrons/cm$^2$-sec).

Figure 14 shows the correction for the time interval between the end of irradiation

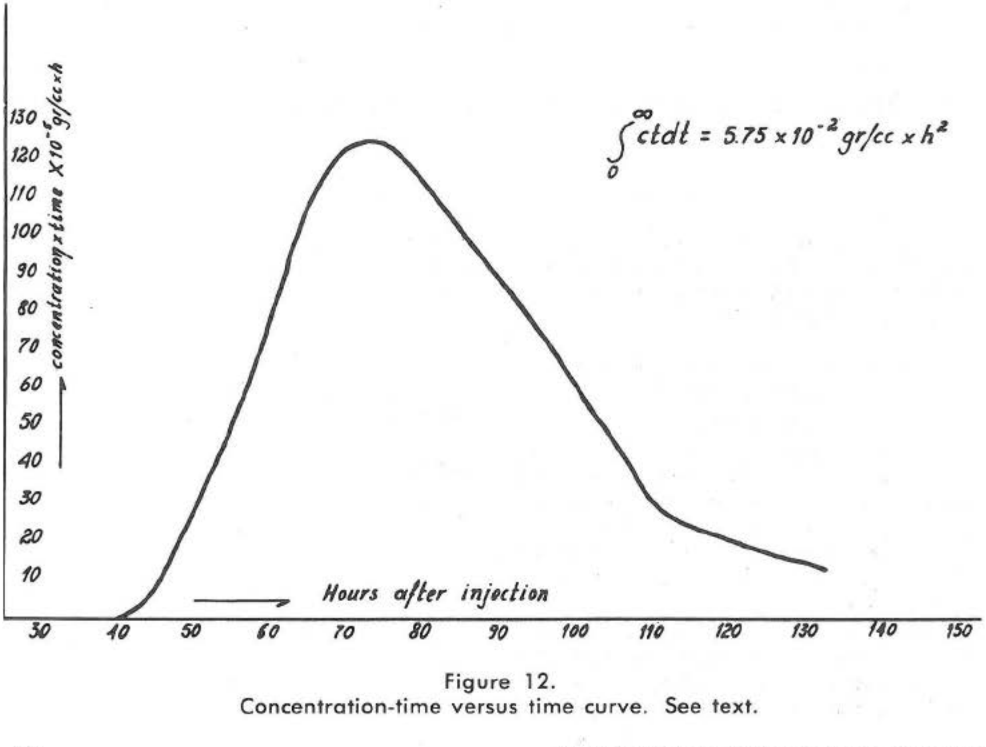

Figure 12.
Concentration-time versus time curve. See text.

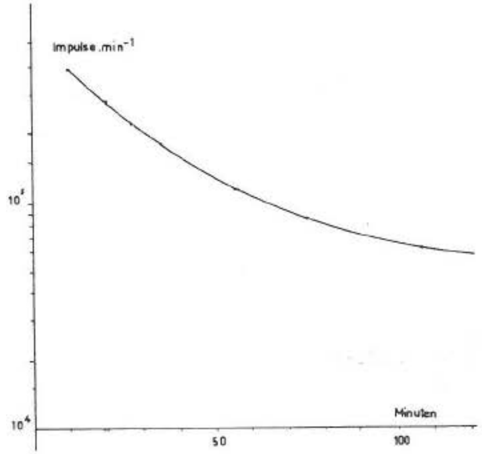

Figure 13.
Radioactivity of 20 ml of $10^{-5}$ normal ammonium bromide solution after irradiation of the reactor (50 min at neutron flux of $0.7 \times 10^{12}$ n/cm$^2$-sec).

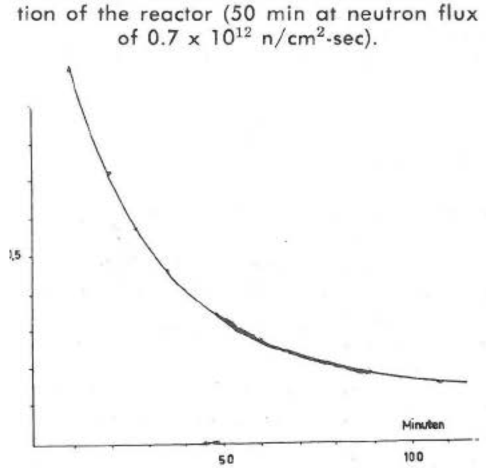

Figure 14.
Correction curve for delay between end of irradiation and beginning of measurement. See text.

and the beginning of radiation measurement. In this plot all disintegration rates are corrected for the same time interval (10 minutes). Water samples without bromine show a small amount of radioactivity after irradiation, and the Compton effect of high-energy radiation also contributes some activity at 0.62 mev. Figure 15 shows the decay curve of a sample which contains no bromine.

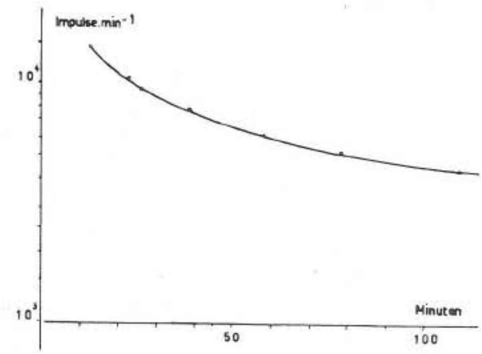

Figure 15.
Radioactivity of pure water after irradiation in the reactor.

Twenty ml fractions of the samples were sealed in polyethylene containers and irradiated with a flux of $0.7 \times 10^{12}$ thermal neutrons/cm-sec for 50 minutes. The water was then poured into flat planchets and the activity was determined with a 2 inch by 2 inch NaI scintillation detector and a single channel analyzer (Tracerlab model SC 76) at 0.62 mev. All samples were measured under comparable conditions.

The count rate was corrected by the values shown in figure 13 (radioactivity due to other nuclides) and normalized (using figure 14) to an activity 10 minutes after the end of irradiation. Twenty ml samples of $10^{-5}$ molar $NH_4Br$ were also irradiated as standards. About 100 samples were analyzed, and the results are shown in figure 16.

The analyses could be performed quickly. It was only necessary to fill the irradiation vessels, prepare the samples for counting, read the counter, and perform a few sample calculations. Every five minutes a sample was removed from the reactor for counting and interpretation and the irradiation of a new sample was begun.

## COMPARISON OF METHODS AND SUMMARY

Each of the methods used in this experiment was successful in tracing the flow from the western slopes of the Buchkogel range

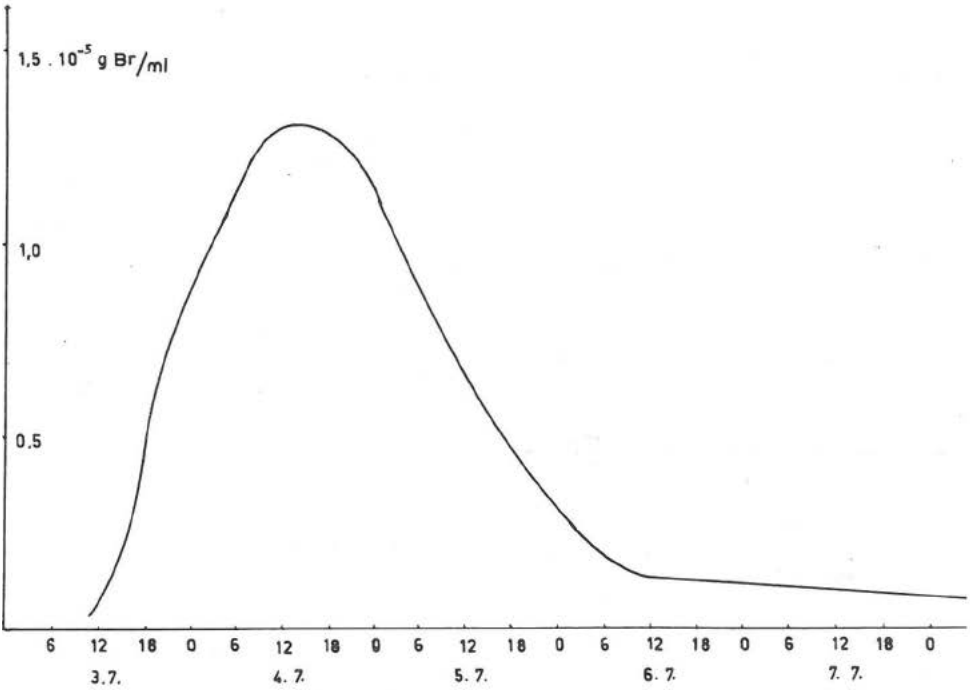

Figure 16.
Bromine content versus time curve for the Bründl Spring.

to the Brundl spring on the east side of the range. Ideally, each of the methods used could be employed in the investigation of other karst water systems. In actual practice, however, each of the methods has certain limitations.

If the area to be investigated is large, with many springs to be watched and long passage times for the water, the use of radioactive isotopes is virtually ruled out, due to the considerable amount of equipment and large numbers of personel needed. In small areas with self-contained water systems, and especially when the water is thought to flow through fine clastic sediments, the radioactive isotopes method could prove quite useful.

When an extensive karst terrain must be investigated, the use of dyed lycopodium spores is still the cheapest and simplest method. The application of five colors allows the simultaneous tracing of the flow from five different swallow holes, and the observation of springs using plankton nets is of impressive simplicity compared to other methods. The greatest drawback to the spore method is its limitations to regions of limestone, dolomite, and gypsum, where the flow is in open conduits. It should be mentioned in this respect that large areas in central, southeast, and south Europe consist of limestone, dolomite, and gypsum terrains (*e.g.,* one-seventh of Austria and one-third of Greece). We have conducted successful investigations with spores in the karst massifs of the Northern Limestone Alps. Difficulties do arise, however, even in limestone regions, when the karst water flows through gravels. It is this fact which makes combined experiments necessary.

The comparative experiment reported in this paper has shown that a combined use of spores and Rhodamine B is of great utility. Uranine will, however, still be given preference in ground-water systems in gravels and clays, inasmuch as clay adsorbs Rhodamine B. The prolongation of the passage of Rhodamine B due to absorption may, however, be useful in tracing rapidly flowing water.

If only qualitative results are needed, samples may be collected at long intervals. If the concentration of the dye at the resurgence is sufficiently high, its presence can be detected by the coloring of cotton fabric suspended in the water. Thus the simplicity of observations favors the use of a combination of lycopodium spores and Rhodamine B.

The activation analysis method also proved successful. The amount of ammonium bromide required for clear proof is appreciably larger than the amount of spores or dye required. It is, however, only one-tenth the quantity of NaCl needed for the chloride tracing. In the area where 35 kg of $NH_4Br$ was introduced in 1963, 500 kg of NaCl was introduced in May 1956 and 300 kg in June 1956. In all of these experiments an excessive amount was used in order to obtain clear passage curves in the comparative tests. Furthermore, it is basic from the point of view of economics to overestimate the amount of material needed rather than to endanger the results of the experiment by not using enough.

The passage curve for the activation analysis method showed that samples need be taken only twice daily for an approximate evaluation. The activation analysis method allows the amount of discharging tracer to be computed with considerable accuracy, and permits a fair estimate to be made of the amount of water in the groundwater system.

Neither of these calculations are possible with the spores or Rhodamine B. The plankton nets intercept only a fraction of the larger resurgences, and although, in our experience, this is sufficient to check the spores and draw a passage curve (because the spores are so well mixed with the water), it is not possible to calculate the quantity of spores which emerges. The calculation of the amount of dye emerging is equally difficult. The dye is continuously being adsorbed underground, and, due to the varying amounts of clay present, behaves differently in systems which are otherwise similar. Another problem is the intensification of color in the water due to the presence of dyed clay particles. These factors prevent any meaningful calculations and are responsible for the overly large estimates of dye concentration in many investigations.

A comparison of the rates of travel of the various tracers shows that the lycopodium spores travel faster than the Rhodamine B dye, the iodine-131, or the ammonium bromide (figure 17 and Table 4). Spores were

**TABLE 4**

| Date | Discharge (1/sec) | Hours From Injection to First Appearance | | | | | Hours From Injection to Passage Peak | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Spores | Cl | Br | Dye | I-131 | Spores | Cl | Br | Dye | I-131 |
| 1956<br>May 12-14 | 16.5<br>constant | | 21½ | | | | | 55 | | | |
| 1956<br>Jun 22-28 | 23<br>constant | 13½ | 19½ | | 13½ | | 19 | 31 | | 31 | |
| 1957<br>Mar 23-25 | 23 init.,<br>later less | 13 | | | | | 33 | | | | |
| 1958<br>May 20-24 | 6<br>constant | 34 | | | | | 49 | | | | |
| 1963<br>Jul 1-12 | 7.5 init.,<br>16 after<br>30 hrs.,<br>then 9 ave. | 33 | | 41½ | 42 | 44 | first<br>peak 39<br>second<br>peak 52 | | 68 | 69 | 78 |

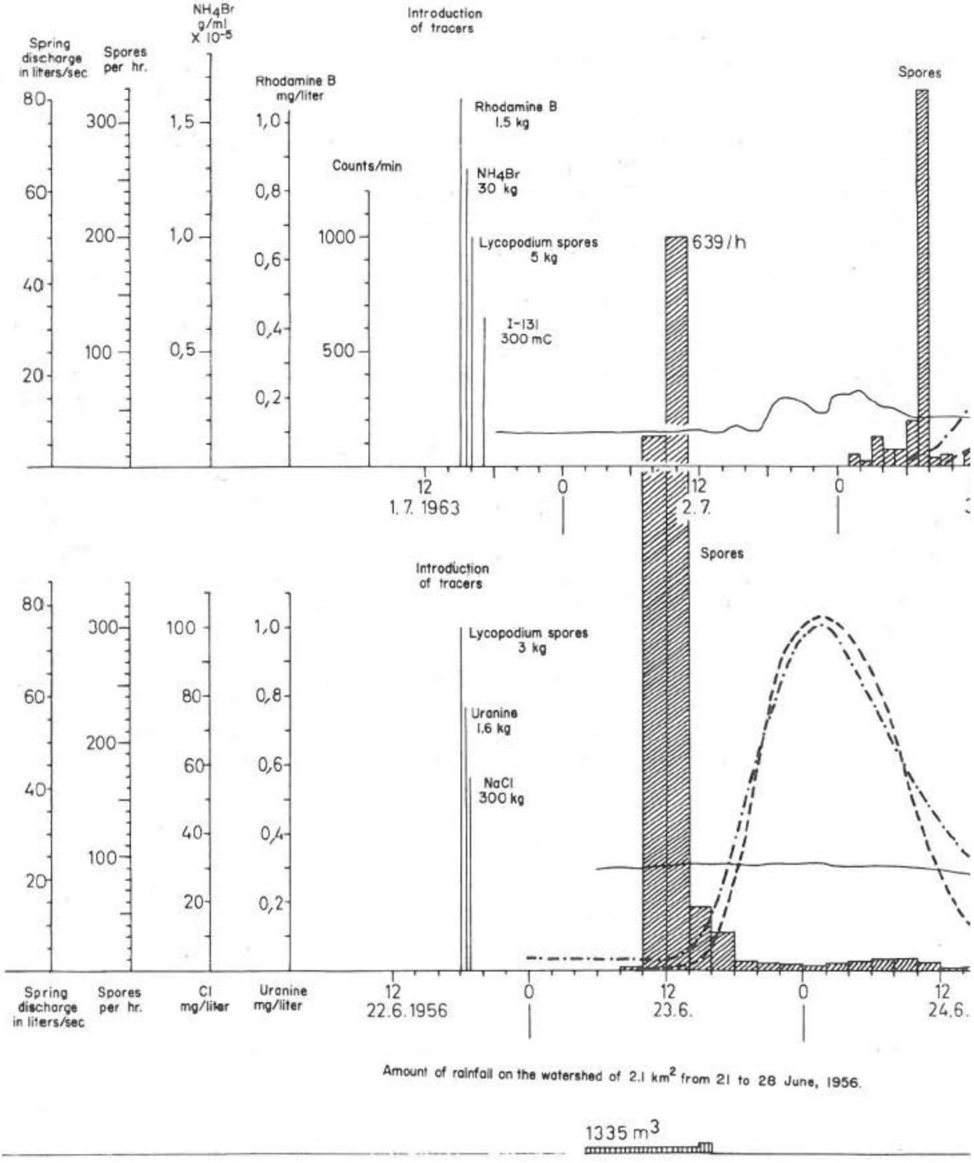

Figure 17.

first detected 33 hours after they were introduced, 8 hours before the appearance of either dye or the bromine (although these substances were introduced one hour before the spores). The passage curve for the spores showed two striking peaks. The first and higher peak occurred 28 hours and the second peak 15 hours before the peaks in the passage curves of bromine and Rhodamine B (which occurred simultaneously). The occurrence of two peaks in the spores is attributed to the temporary rise in discharge. The passage curves of Rhodamine B and I-131 also showed two peaks (figure 17).

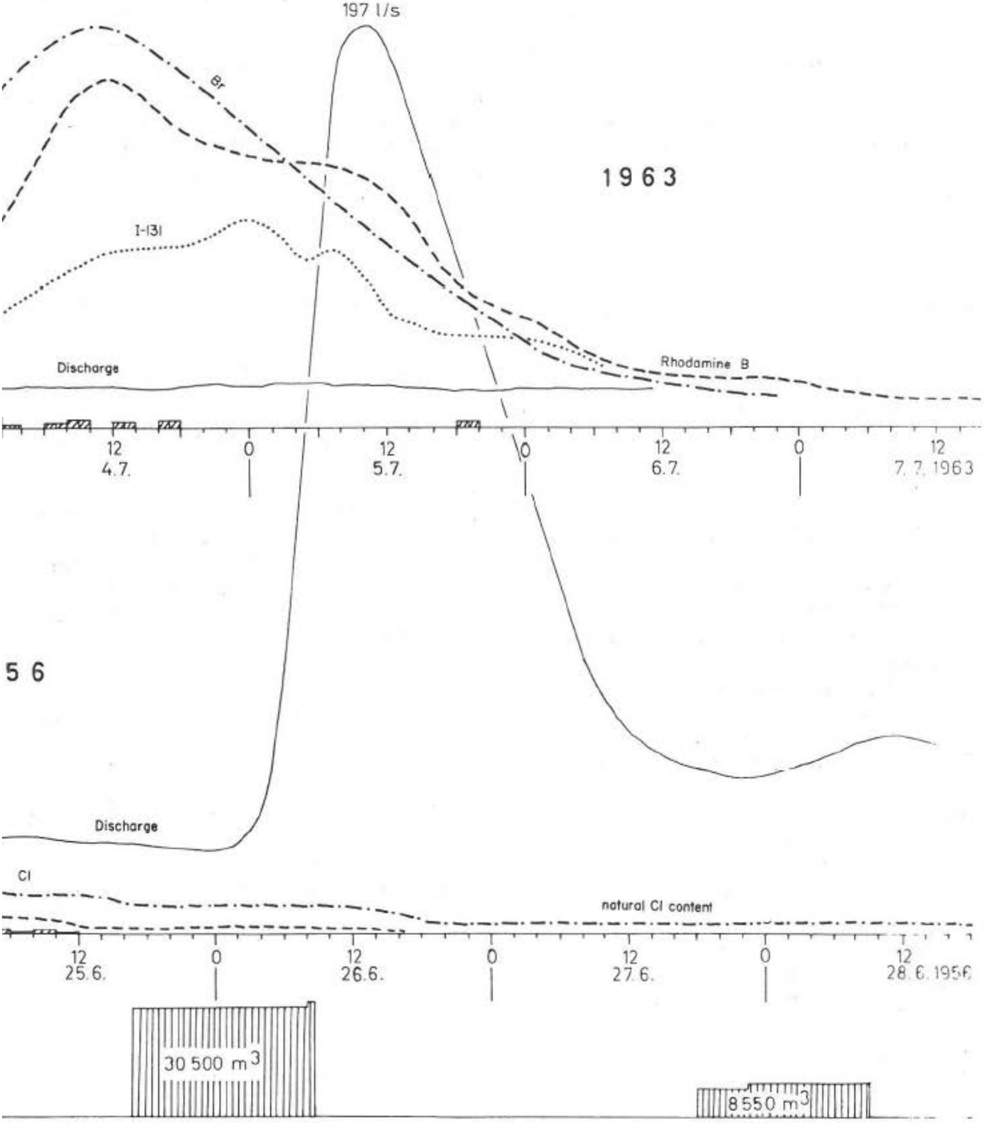

Figure 17.

The passage of the spores had abated by the time of the bromine and Rhodamine B peaks. The same phenomena was observed in June 1956 when spores, sodium chloride, and uranine were used. The interval between the spore and other passage peaks in 1956 was only 12 hours, which may be explained by the larger discharge of the spring (23 l/sec in 1956 versus 10 l/sec in 1963) which shortened the travel time of all the tracers and reduced the time between the peaks. The larger discharge during the 1956 was also probably responsible for the larger fraction of spores recovered in 1956.

Measurements of flow rates with different tracers are not directly comparable. In the investigations which have been conducted so far, the travel time of spores has been the shortest. The travel times for bromine and Rhodamine B have been nearly the same, both with respect to their first appearance and their peak concentrations. Slowest of all has been the I-131. Even taking the later introduction time (about two hours) into account, there is a delay of approximately 12 hours (relative to the bromine and Rhodamine B peaks). These differences are especially striking when it is noted that the first peak of spores occurred 33 hours after introduction while the I-131 peak did not occur until 79 hours after introduction.

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Manuscript received by the editor
26 March 1966