

Modifications of Fluorescein Dye Ground-water Tracing Techniques

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Abstract

Various techniques are reviewed for tracing ground-water in a maturely developed karst aquifer by means of fluorescein dye. These are the methods now in common use by speleologists in the United States. Charcoal indicators are used to detect dye reappearing at all suspected resurgences. They eliminate the need for stationed observers and increase the sensitivity of the test. The power of the method is illustrated with some data from the West Virginia Karst. A spectrophotometer method can be used for positive identification of adsorbed dye.

Introduction

Fluorescein dye has been used to trace the course of subterranean waters for many years. The technique, as it is usually applied, consists of inserting a large quantity of fluorescein in the stream to be tested and stationing observers at all suspected resurgences to await the reappearance of the dye. In most cases, one depends on visual observation of the dye which may cause difficulties if the dye reappears at night. In other cases, the observers collect water samples at regular intervals. These are then either examined in Nessler tubes or by ultraviolet light. The movement of the dye, even in a well-karsted limestone aquifer is likely to be slow and transit times of several weeks are not uncommon. The observers must be prepared to remain on watch the entire time which is very tedious for volunteer observers and very expensive for hired ones.

In spite of its limitations, the fluorescein dye method is still a valuable way of tracing underground water. It is the purpose of this paper to review several modifications of the method which remove some of its inherent objections. These methods have been in use by American Speleologists for a number of years and appear to be satisfactory.

The DUNN Method

The major innovation to the fluorescein method is probably the charcoal detector technique invented by J. R. DUNN in 1957. J. R. DUNN's original description of his method was published in a rather obscure publication and it seems to have escaped notice in spite of being mentioned by J. L. HAAS (1959) in his review of ground-water tracing methods.

The method eliminates the need for continuous observation by replacing the observers of suspected resurgences with small dye-detectors. The detectors adsorb the dye pulse as it passes and hold it until it is elutriated. The collection of the detectors and their examination in the laboratory can be at the convenience of the investigator.

The detectors are constructed from 2 to 4 cm lengths of 5 cm diameter plastic pipe capped with 80 mesh wire screen. Some provision is made for anchoring the detector to the bottom of the stream.

The detectors are filled with 10 to 12 mesh high strength coconut charcoal which acts as the adsorbing medium. The detectors are loosely packed so that water can freely circulate around the charcoal grains.

A charcoal detector is placed in each suspected resurgence to the karst water body and a charge of dye is placed in the sinking stream under examination. A pulse of dye passing through the detector will be adsorbed and held. Laboratory tests have shown that the adsorption of dye is nearly irreversible. In one test performed by J. R. DUNN, a charcoal sample was charged with dye by washing with a one-ppm solution of fluorescein for 15 minutes. The charcoal retained enough dye to yield a positive test after six weeks of further washing in pure water.

When the dye-detectors are collected, the charcoal is removed and placed in small test tubes or a white evaporating dish. The dye is elutriated with a 5% solution of potassium hydroxide in ethanol. The solution is not stirred. If a dye pulse has passed through the detector, a green color will appear on the surface of the charcoal granules.

The dye-detector is much more sensitive to small concentrations of dye in the stream than is a human observer. The initial sharp dye pulse spreads by diffusion (A. N. DIACHISHIN, 1963) and by ponding of the stream. After a karst stream has flowed several kilometers the dye pulse is spread over hundreds of meters of stream reach. Since the entire pulse flows past the detector, the detector integrates the pulse and greatly increases the effective concentration of dye. For this reason, much smaller charges of dye can be used than are necessary for visual detection.

Field studies

The DUNN method has been in use by various American speleologists for about eight years. Some evaluation of results have been reported by T. D. TURNER (1958) who traced a number of streams in the Appalachian Valley karst of Central Pennsylvania. By far the most intensive study has been that of H. ZOTTER (1963, 1965) in the Mississippian Plateau karst of West Virginia.

A sampling of ZOTTER's data is given in Table 1. It should be noted that good results were obtained over distances of three kilometers using a maximum of 200 grams of dye. This sampling was selected from 62 experiments. A number of short distance connections were established using less than 100 grams of dye.

Table 1: Positive ground-water connections in West Virginia Karst
(after H. ZOTTER, 1963, 1965)

Drainage System	Dye Charge	Distance	Nature of Conduit
Dry Creek to Sharp Farm Spring	200 gm	1.8 km	unknown
Beveridge Pit to Overholt Blowing Cave	200 gm	3.9 km	open cave channel with free surface stream
Underground route of Stamping Creek	200 gm	2.7 km	unknown, probably, sub-water table conduit flow
Bruffey Creek Sink to Hughes Creek Cave	200 gm	2.1 km	partly unknown, partly small conduits running pipe-full
Hause Waterfall Cave to Cave Creek Spring	100 gm	3.0 km	partly free surface stream in open cave passage, partly submerged passage
Hills Creek Cave to Locust Spring	200 gm	2.1 km	mostly unknown, probably submerged cave passage

In some cases several tests had to be conducted to conclusively establish a ground-water connection. Best results were obtained under high water conditions. During draughts, the subterranean streams were ponded resulting in much loss of dye through adsorption.

Spectrophotometric determination of fluorescein

The main difficulty reported in the field testing of the dye detector was the problem of recognizing the dye elutriated from the charcoal. A number of tests were inconclusive because it was uncertain whether the faint greenish color appearing on the charcoal surface was desorbed dye or whether it was due to contamination from algae and other natural colorants in the water.

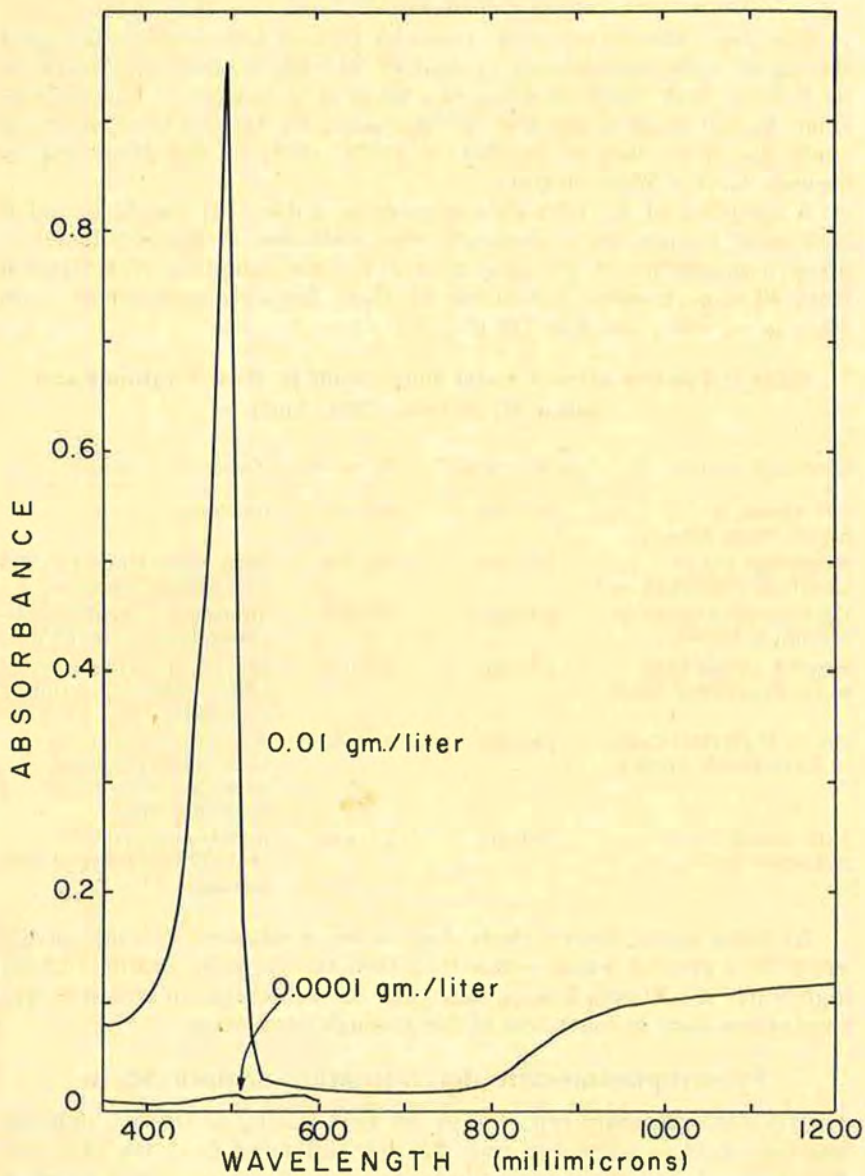


Fig. 1: Optical absorption spectrum of water solution of fluorescein obtained on Beckmann DK 2-A Spectrophotometer in one-cm path length cell.

Fluorescein has a very characteristic absorption spectrum which can be used to identify the dye. The spectrum is shown in Figure 1. There is a single intense absorption band at 495 $m\mu$ with a specific extinction coefficient of 92. The spectrum of the charcoal elutriate is obtained and the presence of this 495 $m\mu$ band used to prove the presence of fluorescein dye. The spectrophotometric test is useful only for the positive identification of the dye; there is no increase in sensitivity. The 0.01 gm/liter solution in Figure 1 is a deep green color and has a very strong absorption band. The 0.0001 gm/liter solution is perceptibly green to the eye in very thick layers and it shows a barely perceptible absorption peak with a one-centimeter path length cell. Thus the sensitivity of the method is about one ppm (0.001 gm/liter) in the elutriate. This corresponds to a concentration at least an order of magnitude lower in the original ground-water.

Fluorescein has a strong green fluorescence at 510 $m\mu$ when illuminated by ultraviolet light and this fact has often been used. Water samples collected by observers were tested with ultraviolet light and the presence of a green fluorescence used to confirm the presence of the dye. To compare the sensitivities of the two techniques, fluorescence spectra were obtained on fluorescein solutions. An 0.01 gm/liter solution could be made to yield a fluorescence peak with about the same intensity as the absorption band. The fluorescence peak of an 0.0001 gm/liter solution was not detectable above background. Thus the sensitivity of the fluorescence test seems to be comparable to that of absorption test.

Future development

Although one may establish ground-water connections by various tracing methods, much information is lost in the way the data are collected. Most of the presently used methods of dye tracing give rather poor estimate of the travel time of the dye. None of the methods give information about the shape of the dye pulse. These are valuable pieces of information because they tell something about the nature of the aquifer.

A device could be built, based on the absorption spectrum of the dye, which would continuously monitor the stream and record the dye concentrations in the water as a function of time. Such a device is sketched in outline in Figure 2. The portion of the instrument which is submerged in the stream, consists of a light source and monochromator, an open area through which water can freely circulate, and a pair of photomultiplier detectors. The light beam is split into two paths. One is passed through a filter which peaks at the strong absorption band of fluorescein. The second is passed through a filter which peaks in a region of the spectrum where fluorescein has very little absorption. The intensities of the two beams are measured by the photomultiplier tubes and

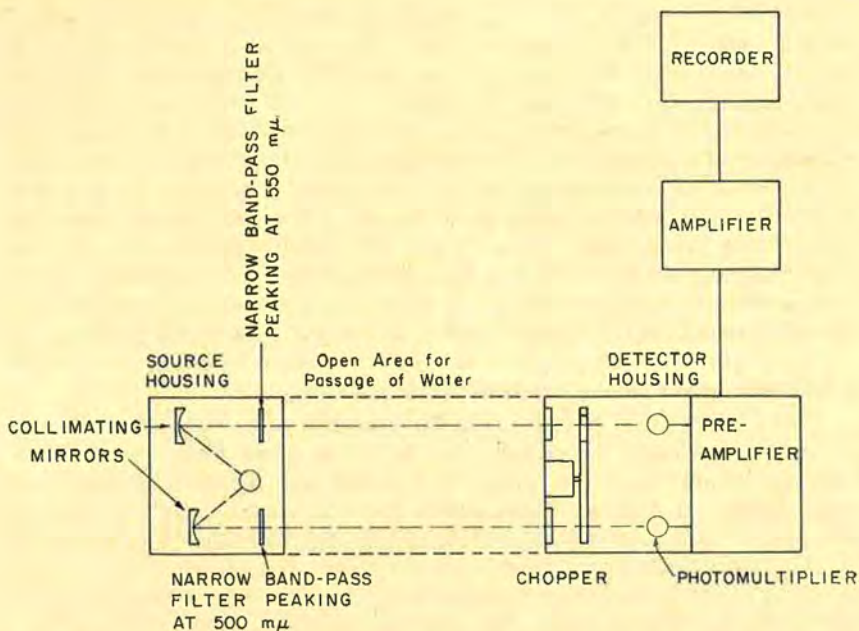


Fig. 2: Schematic drawing of possible optical detector and recorder for dye in streams.

the resulting electrical signals are bucked against each other. The difference signal, if any, is amplified and recorded.

If the water passing through the instrument contains no dye, the intensities of the two beams will be equal and will cancel out delivering a zero signal to the recorder. However, if there is a concentration of dye in the water, light will be absorbed preferentially in the beam containing the 500 mμ filter, and an unbalance signal will be recorded. The strength of the signal will be related to the concentration of dye and thus the recording will provide a concentration versus time plot of the dye pulse. If the time when the dye was injected is known, exact travel times will also be recorded.

This type of device is completely speculative at the moment but might be useful to the development of the dye tracing technique.

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Zusammenfassung

Der Einsatz von Fluoreszeinfarbstoff als Mittel zur Verfolgung des Verlaufes unterirdischer Wasserläufe in Karstgebieten ist ein sehr altes Verfahren. Es leidet unter mehreren Mängeln, die seine Wirkung stark beeinträchtigen und die diese Methode in letzter Zeit unbeliebt gemacht haben. Der ziemlich kostspielige Farbstoff muß, wenn er visuell festgestellt werden soll, in großen Mengen eingesetzt werden. Zweitens müssen an allen möglichen Austrittsstellen des unterirdischen Wasserlaufes Beobachter oder Probenentnehmer aufgestellt und sehr häufig Wasserproben entnommen werden. Das ist äußerst störend, weil es sich dabei um Tage, ja um Wochen handeln kann. Dieser Bericht soll eine Reihe von Verbesserungen vorführen, die von amerikanischen Speläologen an dem Farbmarkierungsverfahren vorgenommen wurden und viele damit verbundene Schwierigkeiten ausschalten.

Die Notwendigkeit, Beobachter aufzustellen und Wasserproben zu entnehmen, wird beseitigt durch das Kohle-Farbstoffdetektor-Verfahren. J. R. DUNN schlug 1957 vor, an allen möglichen Austrittsstellen des unterirdischen Wasserlaufes kleine Detektoren einzubauen, die aus Drahtnetzbehältern von 2 bis 4 cm Durchmesser bestehen, welche mit aktiver Kokosnußkohle gefüllt sind. Wenn der Fluoreszeinfarbstoff an dem Detektor vorbeifließt, wird der Farbstoff von der Kohle adsorbiert und festgehalten. Später werden die Detektoren eingesammelt, die Kohle in eine weiße Verdampfungsschale gelegt und mit einer Ethanollösung von Kalisalz elutriert. Dabei wird jeder vorhandene Farbstoff desorbiert und färbt die Lösung grün. Versuche zeigten, daß die Detektoren 4 bis 6 Wochen ohne Farbstoffverlust im Wasserlauf bleiben können. Dieses Verfahren erhöht auch die Sensitivität des Tests, da der Detektor den ganzen Farbstoff erfaßt und dadurch den Farbstoff aus einem großen Wasservolumen konzentriert.

Das DUNNsche Verfahren ist im Felde durch die sehr ausgedehnten Messungen erprobt worden, die H. ZOTTER von 1960 bis 1964 im Karst von West-Virginia vorgenommen hat. Der unterirdische Verlauf kleiner, versunkener Gerinne wurde auf Entfernungen von 2 bis 6 km verfolgt, wozu nur 100-Gramm-Portionen Farbstoff verwendet wurden.

Der Hauptnachteil des Kohledetektorverfahrens ist die Ungewißheit über den Ursprung blaßgrüner Lösungen, die man aus der Kohle elutrieren kann. Feldversuche zeigen, daß auch Algen und die Vegetation im Wasserlauf eine grünliche Farbe hervorrufen können. Das Fluoreszein kann aber mit Hilfe seines charakteristischen optischen Absorptionsspektrums festgestellt werden. Der Farbstoff hat ein einziges Absorptionsband bei 490 Mikromikron mit einem spezifischen Extinktionskoeffizienten von 92. Eine Lösung, die dem Auge gerade noch als grünlich erfaßbar ist (0,0003 mg/l) ergibt ein meßbares Absorptionsmaximum und bestätigt dadurch die Herkunft der Farbe. Auch der Einsatz der Absorptionsspektroskopie ermöglicht quantitative Messungen und bahnt den Weg für automatisch aufzeichnende Instrumente.

Résumé

L'emploi de la fluorescéine comme colorant pour suivre le cours d'eaux souterraines dans des régions karstiques est un procédé très vieux. Il souffre de plusieurs défauts qui, tout en portant gravement atteinte à son efficacité, ont récemment rendu impopulaire cette méthode. Pour être constaté de façon visuelle, ce colorant assez coûteux doit être employé en grandes quantités. Ensuite, il faut qu'à toutes les sorties éventuelles du courant souterrain d'eau soient placés des observateurs ou des personnes chargées du prélèvement d'échantillons; des échantillons d'eau doivent être prélevés très souvent. C'est extrêmement fâcheux parce que, en l'occurrence, il peut s'agir de jours, même de semaines. Ce résumé va présenter plusieurs améliorations qui, accomplies par des spéléologues au procédé de marquage par colorants évitent beaucoup de difficultés qui en résultent.

Grâce à la méthode de détection par charbon et colorants, il n'est plus besoin de placer des observateurs ni de prélever des échantillons d'eau. En 1957, M. J. R. Dunn proposa d'installer à toutes les éventuelles sorties du courant souterrain d'eau de petits détecteurs constitués par des récipients en filets de fil de fer ayant un diamètre de 2 à 4 cm qui seront remplis de charbon actif de noix de coco. Le colorant de fluorescéine passant le détecteur est absorbé et retenu par le charbon. Plus tard, les détecteurs seront ramassés, le charbon sera mis dans un bol d'évaporation et extrait par le moyen d'une solution d'Ethanol de potasse. En même temps, tout colorant existant sera dégagé tout en teignant la solution en vert. Des expériences ont démontré que les détecteurs peuvent rester dans l'eau pendant une période de 4 à 6 semaines sans perdre de colorant. Ce procédé augmente aussi la sensibilité de l'essai, puisque le détecteur embrasse le colorant tout entier et, par conséquence, concentre le colorant partant d'un gros volume d'eau.

La méthode de Dunn a été essayée sur le terrain au cours des mesures de grande envergure effectuées de 1960 à 1964 par H. ZOTTER dans la région karstique de Ouest-Virginia. On a suivi, à des distances allant de 2 à 6 km, l'écoulement souterrain de petits ruisseaux qui se sont enfoncés dans le sol. A cet effet, des portions de colorant à 100 grammes seulement ont été employées.

L'inconvénient principal de la méthode de détection au charbon est l'incertitude sur l'origine de solutions vertes pâles qu'on peut extraire du charbon. Des expériences effectuées sur le terrain montrent que des algues aussi, ainsi que la végétation dans le cours d'eau peuvent créer une couleur verdâtre. La fluorescéine, cependant, peut être constatée grâce à son spectre d'absorption optique qui lui est propre. Le colorant a une seule bande d'absorption à 490 millimicrons avec un coefficient d'extinction spécifique de 92. Une solution que l'oeil peut tout juste constater comme verdâtre (0.003 mg/l) présente un maximum d'absorption mesurable, prouvant ainsi l'origine de la couleur. L'emploi de la spectroscopie d'absorption permet également des mesures quantitatives et ouvre la voie aux instruments enregistrant automatiquement.