6.3. RESULTS WITH FLUORESCENT TRACERS

6.3.1. Analytical Procedures

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Analyses in the HMZ laboratory, Slovenia

The concentration of uranine was determined by scanning the emission spectra on the fluorescence spectrophotometer HITACHI F-4500. The samples had been kept in a dark place at room temperature before the analysis took place. Scanning of the emission spectra was performed by the method of simultaneously changing excitation and emission wavelengths with the constant difference of 25 nm for uranine analyses (BEHRENS 1971, 1973) and the constant difference of 105 nm for pyranine. All spectra were scanned by the same conditions: scan speed 240 nm/min, slit EX/EM 10 nm/10 nm, photomultiplier voltage 950V. The uranine concentrations were measured at pH 10, after addition of EDTA, while the pyranine concentrations were measured at pH 4.5-5.0 after addition of acetate buffer solution (BEHRENS, 1986, 1988). For the preparation of standard solutions with the reference samples unchlorinated tap water was used. Wavelengths of emission maximums and detection limits of fluorescent dyes are given in Tab. 6.6.

Tab. 6.6: HMZ Laboratory: Emission maximum and detection limit of the fluorescent dyes applied in the framework of the 7th SWT.

Tracing experiment	Dye	Emission maximum (nm)	Detection limit (ppb)
1993 - October	uranine	512 ± 4	0.0008
1994 - April	uranine	512 ± 4	0.0008
	pyranine	494 ± 3	0.03
1995 - August	uranine	512 ± 4	0.001
	pyranine	494 ± 3	0.01
1995 -October	uranine	512 ± 4	0.0009
	pyranine	494 ± 3	0.02

The obvious variation of the detection limits for the various experiments was caused either by the variability of the injected tracers, which have been provided by several members of the ATH or by the status of the instrument.

In the HMZ the collected samples were measured almost immediately after they arrived in the laboratory. Depending on the delivery of the samples the time after sampling ranges between 1 and 14 days.

Analyses in the AGK, IHG and GSF Laboratories

As described in the above chapters the tracer samples were mostly taken by automatic samplers provided either by HMZ, by UBA, or by IZRK. The service of the samplers was carried out by IZRK, the samples have been transported at first to the Karst Institute in Postojna, stored and then sent to the individual institutes for further analysis. The Tab. 6.7 may serve as an example for a detailed documentation, which seems to be necessary to collect as much information as possible for the following evaluation. This is important in all cases where results are suspicious to be not correct, because of possible bad storage conditions and adsorption or decay processes during storage.

Comparable to the described methodology of HMZ all the other laboratories got a small amount of reference material as a standard for the calibration of analytical instruments. How to handle the reference material was the responsibility of each laboratory according to common agreement on the used analytical procedure. But there was no previous interlaboratory testing of the used methods and their procedural details.

All three laboratories analysed the samples by fluorescence spectrometry with synchronous-scan-method. For uranine a $\Delta\lambda$ of 25 nm was used after alkalising samples and standards with EDTA for establishing a constant pH-value of the testing sample combined with appropriate complexing of carbonates to avoid their possible precipitation. Pyranine was measured with a $\Delta\lambda$ of 105 nm procedure after adding an acetate buffer solution to establish a pH value of 4.5.

Beside water samples about 400 charcoal bags were used to observe a possible tracer recovery. The processing of the charcoal bags was solely performed in the AGK laboratory. The charcoal bags are processed by extracting the fluorescent tracers with mostly organic solvents. The used mixtures were pH-controlled for an optimum performance. After the extraction the samples were analysed in the above mentioned synchronous-scan method.

Tab. 6.7: Example (second experiment, sampling at the Vipava springs) for delivery of samples and the time delay between sampling and analysis. As the time delay grows a possible alteration of sample properties should be taken into consideration. From this point of view it is recommended to document date and time of sampling, delivery and analysis.

Lab	Storage Conditions	Sampling Period	Delivery to Lab	Analysis
IHG	dark, room temp.	4/3 (940416-940420)	940424	940425
IHG	dark, room temp.	4/3 (940420-940503)	940505	940509
IHG	dark, room temp.	4/3 (940503-950513)	940518	940519
IHG	dark, room temp.	4/3 (940513-940626)	040712	940713
IHG	dark, room temp.	4/3 (940630-940728)	date missing	940824
IHG	dark, room temp.	4/8 (940416-940420)	940424	940425
IHG	dark, room temp.	4/8 (940420-940425)	940505	940511
IHG	dark, room temp.	4/8 (940425-940503)	940505	940516
IHG	dark, room temp.	4/8 (940503-940513)	940518	940519
IHG	dark, room temp.	4/8 (940513-040628)	940712	940712
IHG	dark, room temp.	4/8 (940630-940728)	date missing	940824