Analusis, **1999**, *27*, 541-543

Fluorescent UV dye: A particularly well-suited tracer to determine residence time distributions of liquid phase in large industrial reactors

H. Muhr, J.P. Leclerc and R. David

LSGC-CNRS/ENSIC-INPL, 1 rue Grandville, BP. 451, 54001 Nancy Cedex, France

Abstract. Fluorescent tracers are tested to determine Residence Time Distributions of liquid phase in large industrial reactors. The 1-naphthalenesulfonic acid, which absorbs only in the UV area, is selected for aqueous liquid phase. It is a highly soluble, non-bleaching, easy to supply, inexpensive and non-toxic compound. It can be detected at very low concentrations by fluorescence spectrometry.

Key words. fluorescent UV dye – residence time distribution – tracer – industrial reactor.

Introduction

Residence Time Distribution (RTD) measurement is very often used to yield a simple but sufficient hydrodynamic model for industrial reactors [1]. The main difficulty is to select an adapted tracer and the relevant detector. All types of substances can be used as tracers as long as the tracer response may be assumed to vary linearly with concentration. Experimental constraints have been first detailed by Danckwerts [2] and later by many others authors [3, 4].

When RTD is to be determined directly in a large industrial reactor during the production phase, the tracer should not interfere with the running process and not alter the quality of the manufactured product (pollution, change of color, change of texture). This is especially critical for an industrial under strict obligations of quality norm (ISO 9002 for example). Moreover, the task is complicated for multiphase reactors wherein the tracer of one phase should not adsorb on neither react with the solid phase.

This paper deals with the selection of a tracer adapted for the determination of RTD of liquid phase in large industrial crystallizers. This tracer has to fulfill defined requirements, one of them being not to adsorb on the solid phase. Moreover, the tracer must be colorless, highly soluble, non-bleaching, inexpensive, easy to supply and non toxic.

Criteria determining the choice of the tracer

Despite numerous advantages (small injection, easy detection without sampling directly through the walls, rapid response time, good selectivity and good sensitivity) radioactive isotopes should be eliminated because of financial costs, administrative authorization and public acceptance. Classical salts, such as sodium chloride, are not suitable, because the volume needed for injection is too much for further detection; moreover, impurities will reach a too high value in the solution and in the crystals. Other substances, such as indium or lithium salts, the detection levels of which are very low, are not suited too, because of a high background noise in the solution. Fluorescent dyes in the visible range, which fulfill all other requirements, are not suitable too, because the crystallized product would be colored. UV dyes (azuring substances), which do not absorb in the visible, have been preferred. The properties of some UV fluorescent dyes have been accurately described by Viriot and André [5].

Spectroscopic characteristics

A fluorescent substance can be used as a tracer only if its molar extinction coefficient and its quantum yield of emission are as high as possible. The minimum detectable concentration then appears to be inversely proportional to the width at half peak height of the fluorescence spectrum.

Solubility

The substance, which will be used in aqueous systems, must obviously be highly soluble in water. Although analysis of the fluorescence allows titration of microquantities, this does not imply that low solubility should be satisfactory. For large industrial reactors, we have to inject high concentrations of fluorescent tracers locally. In order to inject the tracer under favorable conditions, the tracer should be used in very

*Correspondence and reprints.
Received March, 16, 1999; revised May 19, 1999; accepted June 1, 1999.

Article available at http://analusis.edpsciences.org or http://dx.doi.org/10.1051/analusis:1999131

concentrated solutions. Moreover, the low solubility of a substance, an expression of its tendency to leave the aqueous phase for the solid phase, reveals as a consequence its ability to adsorb on solid surfaces. We must therefore expect that most weakly soluble substances are strongly adsorbed, and hardly therefore satisfy this criterion for tracing. The fluorescent organic molecules are generally insoluble or slightly soluble in water. Solubility being conferred by an ionic structure, it is often necessary to carry out an appropriate chemical treatment such as sulfonation.

Stability

Since in numerous cases the tracers dissolved in the solution will have a relatively long time to travel before reaching the detector, it must be stable to light during 4 to 5 times the space time in the reactor and even more if the measurements must be carried out later in a laboratory far from the sampling place. Various observations show that for such kind of tracers, the photodegradability should be considered (e.g. fluorescein) (5).

Cost and supply

Although not of paramount importance, for the cost of a tracer only represents a small part of the total cost of an operation, the new tracers should not be overpriced with reference to tracers currently used.

Toxicity

This criterion is of obvious importance. Of course the repetitive character of calibrations and their extents exclude any substances that may have a harmful effect on the manufactured product and on environment.

Selected tracer and discussion

The 1-naphthalenesulfonic acid is one of the fluorescent UV dyes selected as a tracer (naphthalene is insoluble in water, but should be suitable for organic systems). The 1-naphthalenesulfonic acid used is a MERCK product, and its quality is “for synthesis”.

This dye possesses the spectroscopic properties required as stated previously. Dissolution in permuted water is very easy, with solubility values higher than 100 g/L at room temperature. No significant adsorption is registered with the solid phase of the reactor (white crystals in the present case). No degradation is observed after several hours, and it may be considered stable to light. Lastly with requirements, this product is non-toxic and colourless and thus produces no pollution and no colour, neither to the suspended solids nor to the solution. Hence, all criteria mentioned before are fulfilled when using 1-naphthalenesulfonic acid as a tracer.

Measurement of acid concentration by UV absorption should be avoided, because of the existence of interference between acid and aqueous medium. A more sensitive measurement may be obtained by fluorescence. By exciting the acid solution at 280 nm, a specific fluorescence of the acid appears at 330 nm [5]. The 1-naphthalenesulfonic acid is easily detected with a spectrofluorimeter at very low concentrations. Figure 1 illustrates an emission spectrum of 1-naphthalenesulfonic acid solution with a concentration of 10^{-5} M in mother liquid of the studied crystallizer (i.e. a saturated solution of the crystallized product). In practice, maximum emission is slightly higher than the expected value of 330 nm. Figure 2 shows the linearity between the signal and the concentration in the whole range tested. This linearity allows recording the dye concentration on-line or off-line and gives to the tracer the same advantages than radioactive isotopes for data acquisition. The limit of detection with the fluorescence spectrometer used is obtained when dye concentration is lower than 10^{-7} M. At this level, a slight difference is observed between the emission spectra of mother solution with and without the dye. Thus, for a better accuracy a more concentrated solution has to be used. A rapid estimation of the mass of acid required for one injection in a 60 m^3 industrial crystallizer indicates that 12.5 g of 1-naphthalenesulfonic acid should be injected which would cost about 20 US $ (18 Euro).

This tracer has been successfully tested in a Krystal-Oslo crystallizer. The tracer investigation has been carried out without any disruption nor trouble of the production of the white crystals. Unfortunately, due to the confidentiality of the project, the full description of the crystallizer, the experiments and the RTD model interpretation can not be published. However, the description given in this paper allows one to carry out similar tracer experiments in any other crystallizer and of course in any other industrial reactor. The only pre-request is to verify that the tracer is not adsorbed on the solid phase.

Finally, UV dyes will perhaps be one of the best industrial tracers for tomorrow. They offer the same advantages than radioactive substances, at lower cost, without any care for people, for the environment and for the manufactured product.

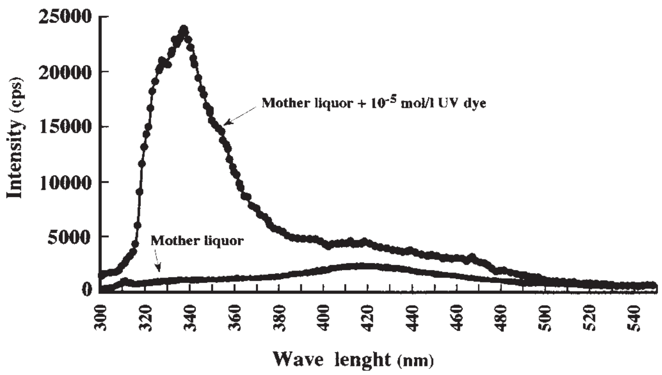

Fig. 1. Emission spectra of an 1-naphthalenesulfonic acid solution at a concentration of 10^{-5} mol L^{-1} in the mother liquid of the crystallizer.

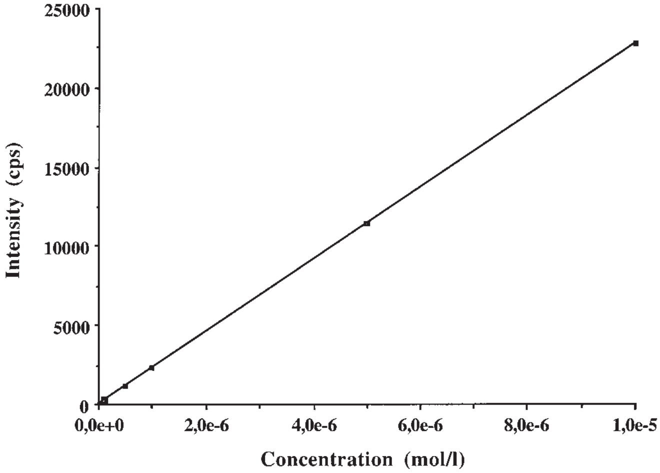

Fig. 2. Linearity between response and dye concentration.

Acknowledgments

This work was supported by Elf-Atochem and the authors are grateful to J.M. Bossoutrot and F. Garcia for their help.

References

1. Leclerc, J. P.; Detrez, C.; Antoine, B.; Schweich, D. *Rev. Inst. Franç. Pétr.* **1995**, *50*(5), 641-656.
2. Danckwerts, P. V. *Chem. Eng. Sci.* **1953**, *2*, 1-18.
3. Villermaux, J. In *Génie de la réaction chimique : Conception et fonctionnement des réacteurs*, Lavoisier Tec. & Doc., 2[e] éd., 1993.
4. Dudukovic, M.P. In *Chemical reactor design and technology*, NATO ASI series, Hugo I. Ed. de Lasa, 1986.
5. Viriot, M. L.; André, J. C. *Analusis* **1989**, *17*(3), 97-111.