STUDIES ON MIXING. XXXIII.*
CONTINUOUS SAMPLING OF DISPERSION OF IMMISCIBLE LIQUIDS

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Received November 17th, 1970

A device is described for photographic continuous sampling of dispersion of immiscible liquids. The problem of proper timing of sampling is investigated too. On several dispersion experiments it is shown that the accuracy of systematic sampling, which is easily realizable with our device, is not inferior to a simple random sampling. This finding may be regarded as a proof of suitability of the proposed method.

In the study of the mechanism of dispersion of immiscible liquids and analysis of the behaviour of dispersion equipment the need arises for a suitable experimental method providing a time sequence of samples of the dispersion. This is one of the typical problems arising in the experimental study of any random process with time parameter, which are often encountered in chemical engineering practice. We shall deal with a case when the evaluation of the particle size distribution in the dispersed phase from the samples is requested. The samples are taken in a selected subregion of the disperser so as to obtain local values of the distribution. The method of direct photographing[1] was selected as the one satisfying these requirements.

ANALYSIS OF THE PROBLEM

Selection of Experimental Technique

The size of droplets in common dispersions (*e.g.* at liquid extraction, suspension polymerization, biochemical technology *etc.*) ranges often from 10^{-3} to 10^{1} mm. The droplets move at velocities reaching several meters per second in the order of magnitude. To obtain photography with a sharp image of the droplet under these conditions necessitates short exposure time.

Let us denote the photographed droplet by A (Fig. 1). The droplet is moving at a velocity c parallel to the principal optical plane, ϱ. Among the focal distance, f,

* Part XXXII: This Journal *37*, 241 (1972).

the object distance, u, and the image distance, v, there is a relation[2].

$$(u - f) . (v - f) = f^2 . \tag{1}$$

Exposure t is determined by the condition stipulating that the trajectory of the object on the picture must not exceed the limit of admissible lack of sharpness b. In macrophotography on small format the latter is usually taken as $b = 0{\cdot}05$ mm. From simple considerations following from Fig. 1 we obtain relation $c/c' = u/v$. The trajectory of the object on the picture equals $b = c't$. For the exposure follows from these relations condition $t < bu/cv$. Expressing the object distance from Eq. (1) we obtain:

$$t < \frac{b}{cv}\left(\frac{f^2}{v - f} + f\right). \tag{2}$$

Condition (2) is evaluated numerically for several cases of practical importance: *a*) Photography on 6×6 cm formate and 1 : 1 magnification ($f = 80$ mm, $v = 156$ mm); *b*) Similar conditions, 2 : 1 magnification ($f = 80$ mm, $v = 228$ mm); *c*) Photography on 36×24 mm formate and 4 : 1 magnification ($f = 50$ mm, $v = 250$ mm).

The velocity of the droplet is taken as $c = 1$ m/s. For these cases we get from Eq. (2)

$$t_a < 53\ \mu s\,, \quad t_b < 27\ \mu s\,, \quad t_c < 13\ \mu s\,.$$

Exposures in this range pertain to photography with a flash or to high speed motion picture photography. The use of a common still picture camera with a flash is not feasible for continuous picture taking owing to the desirable short time between individual shots. The use of a high-speed camera would require the frequency of about 1000 frames per second to achieve the mentioned exposures (assuming that the exposure is one tenth of the inverse of the frame frequency). If we are interested in sampling in a longer period of time (which is quite common) this technique is not suitable either. These considerations stimulated an effort to work out an experimental

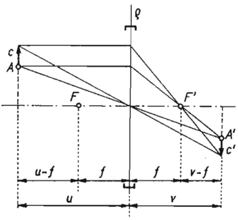

FIG. 1
Determination of Exposure

apparatus which will be described below. The basic idea is to get a set of pictures taken with requested short exposure during sufficiently long time period. In this case also the question becomes that of the distribution of the time instants for individual pictures within the whole observation period. A solution to that is given in the next paragraph.

Distribution of the Samples in Time

Let us investigate now a problem in which one of the results of the theory of sampling survey can be applied. It is a good illustration of expediency and fruitfulness of application of statistical methods to the study of dispersion. Let us assume first that a stationary population* is sampled and investigate suitable time distribution of the samples. There are basically two ways how to select the length of time interval between single shots, $\Delta\tau_s$: uniformly ($\Delta\tau_s$ is constant), or randomly ($\Delta\tau_s$ is a random variable). The first method is the so called systematic sampling, while the second is the simple random sampling. We shall investigate the question of choice between these methods and use some properties of the systematic sampling described for instance in the book by Cochran[3]. A dispersion of two immiscible liquids is characterized for this purpose by the average size of the particle, $\bar{x}_i$, in the i-th picture. On evaluating the photographic picture[1] we obtain a vector of interval frequencies, $\{n_j\}$, assigned to the vector of particle sizes, $\{x_j\}$. By repeated sampling we obtain a matrix of the frequencies, $\|n_{ij}\|$, of the $k \cdot l$ dimension (index i denotes the sample, j the interval of size). A sample characterized by $\{n_j\}$ we shall term the partial sample, and the sample $\|n_{ij}\|$ the systematic sample. The classified distribution of frequencies, which is necessary for evaluation of the drop size distribution from the pictures, is assumed. Another assumption (not restricting) is that the frequencies in all samples are distributed into the same size intervals. That means the independence of $\{x_j\}$ on i. With this structure of the data, the relationships presented in paper[3] need some modification.

The size of the sample will be defined as:

$$n_i = \sum_{j=1}^{l} n_{ij}\,, \tag{3}$$

the mean of the partial sample is

$$\bar{x}_i = (1/n_i) \sum_{j=1}^{l} n_{ij} x_j\,, \tag{4}$$

the size of the systematic sample is

$$N = \sum_{i=1}^{k} \sum_{j=1}^{l} n_{ij}\,, \tag{5}$$

* For the case of a population with a linear trend it is known[3] that the systematic sampling is always more accurate than the simple random sampling.

the mean size of the droplet in the systematic sample is

$$X = (1/N)\sum_{i=1}^{k} n_i \bar{x}_i\,, \tag{6}$$

the sample variances of partial samples

$$s_i^2 = (\sum_{j=1}^{l} n_{ij}(x_j - \bar{x}_i)^2)/(n_i - 1)\,, \tag{7}$$

the sample variance of the systematic sample

$$S^2 = (\sum_{i=1}^{k}\sum_{j=1}^{l} n_{ij}(x_j - X)^2/(N - 1)\,, \tag{8}$$

the mean of the partial variances

$$\overline{s^2} = (\sum_{i=1}^{k} s_i)/k\,, \tag{9}$$

the correlation coefficient of pairs of deviations from the mean of the systematic sample

$$\varrho = (\sum_{i=1}^{k}\sum_{j<u} n_{ij}n_{iu}(x_j - X)(x_u - X))/(S^2 \sum_{i=1}^{k}\sum_{i<u} n_{ij}n_{iu})\,. \tag{10}$$

Expression $\sum_{i=1}^{k}\sum_{j<n} n_{ij}n_{iu}$ in the denominator of Eq. (*10*) denotes the number of different values in the numerator and $u = 2, 3, \ldots l$.

On taking the value of the variance of the sample mean as a measure of the accuracy of the sampling method it may be proven[3] that the systematic sample is more accurate than the simple random sample then, and only then, if

$$\overline{s^2} > S^2\,. \tag{11}$$

The variance of the systematic sample equals

$$\operatorname{var}(X) = (S^2/n)((N - 1)/N + (n - 1)\varrho)\,. \tag{12}$$

In the last equation it is assumed that the size of the partial sample, n, is constant. From this equation it can be further seen that even a small positive correlation of deviations according to Eq. (*10*) may have a marked effect on reliability of the mean of the systematic sample. The verification of accuracy of the systematic sample is based on Eq. (*11*) and its results are summarized in Table I.

TABLE 1

Sampling Condition and Results

Run No	$\Delta\tau_s$ s	k	n^a	$\bar{s}$ by Eq. (*9*)	S by Eq. (*8*)	ϱ by Eq. (*10*)
1	5	32	51	0·09775	0·09756	—0·06122
2	5	59	13	0·10861	0·10821	—0·07833
3	5	42	32	0·10176	0·10123	—0·05872
4	5	97	8	0·15464	0·15345	—0·03116
5	5	54	11	0·20503	0·20881	—0·05334
6	10	31	14	0·19684	0·19770	—0·04857
7	5	150	11	0·19873	0·19922	—0·06447
8	5	200	19	0·13304	0·13164	—0·04029
9	5	100	15	0·10978	0·10683	—0·00714
10	5	100	15	0·13240	0·13066	—0·04325
11	5	100	15	0·21266	0·21116	—0·05660
12	5	100	16	0·16023	0·15940	—0·04929
13	5	100	31	0·13847	0·13809	—0·05766
14	5	100	23	0·08408	0·08361	—0·08111

[a] Mean value for k-samples (was not constant).

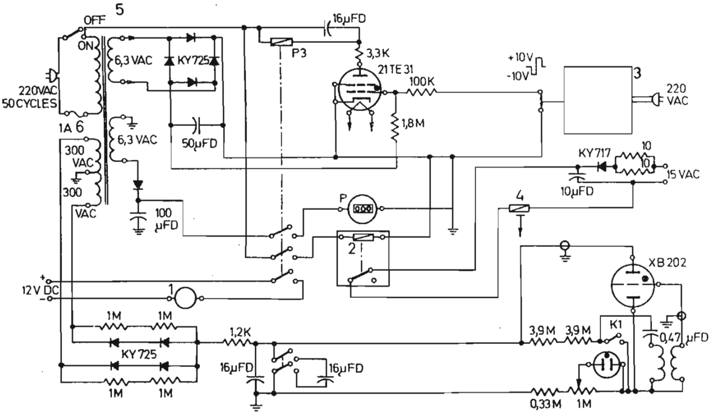

FIG. 2

Scheme of Equipment for Continuous Sampling

EXPERIMENTAL AND RESULTS

An AK-16 (Ihagee Dresden) motion picture camera with an equipment for single shots was used. An XB 80-22 (Pressler) discharge tube was used as a source of flash light. A special device, the scheme of which is shown in Fig. 2, was designed for continuous picture taking. The device works quite automatically and it is controlled by a low frequency voltage pulse source *3* through a thyratron 21 T 31. This ensures stability of the interval between individual shots, $\Delta\tau_s$, as requested at systematic sampling. During one working cycle the motor of the camera *1* is turned on and off by a relay P 3 and the time-delay relay *2*, and an electromagnet *4* sets in operation the device for individual shots. Each shot is registered on a telephone counter *P*. Switching off the motor at a long-term measurement is necessary to avoid its overheating. The energy of the flash is 2 J or 4 J, duration of the flash is about 10 μs. The minimum time between two flashes is about 0·5 s. The flash is synchronized with the camera shutter by a contact *Kl*. The device works reliably, it is assembled from commonly available parts and instruments and fully meets requirements put on it in experimental study of dispersion mentioned in the introduction of this paper.

The verification experiments aimed at solution of the problem of time distribution of samples were carried out in cylindrical vessels 170 and 300 mm in diameter without baffles, with turbine stirrers of different diameters and with an propeller (Experiments No 5 and 6). The frequency of the stirrers ranged between 170 and 240 r.p.m. A mixture of cyclohexane and tetrachloromethane (density 1 032 kg m^{-3}, interfacial tension 48·5 dyn cm^{-1} and viscosity 0·9 cP — all properties at 20°C) was being dispersed. Water was used as continuous phase; the volume fraction of the dispersed phase was 0·05. Conditions of sampling are summarized in Table I. For more detailed information on dispersion experiments the reader is reffered to the earlier paper[1].

An analysis of the results summarized in Table I has shown that inequality (*11*) was satisfied in most of the cases and, consequently, the accuracy of the systematic sampling is not lower than that of a simple random sampling (the latter is usually recomended in statistical studies). In accordance with this a small negative value of the correlation coefficient was found.

It may be concluded that the systematic sampling at continuous sampling of a random process in time is always more easily realized than the random one. From this fact follows also the importance of our study which may be applied also to other chemical engineering research problems.

LIST OF SYMBOLS

c velocity of droplet in flowing dispersion
c' velocity of droplet on the picture
f focal distance
n frequency, size of sample
N size of systematic sample
s sample variance
S sample variance of the systematic sample
t exposure
u object distance
v image distance
x size of droplet
X mean size of droplet in systematic sample

ϱ correlation coefficient, principal optical plane
τ time
$\Delta\tau$ time interval

Subscripts

$\bar{a}$ mean value of quantity a
i partial sample
j interval of droplet size
k number of partial samples
l number of size intervals
s sample in general
u variable upper limit in Eq. (*10*)

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Translated by V. Staněk.