Greek Letters

γ = constant in growth rate expression, Equation (7)
Γ = gamma function
ρ = crystal density
ψ = dummy variable in Equations (10) and (15), $(1 + \gamma L)^{1-b}$
τ = residence time

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Hydrodynamics of Drop Formation From a Hydrocarbon Film Around a Sphere Placed in a Moving Aqueous Phase

The study of the coalescence of secondary dispersions passing through a granular packing has led to the consideration of drop formation from a hydrocarbon film around a single sphere placed in the flux of an aqueous phase. An analogue mock-up study led to a mathematical model for relating the diameter of the drop to various parameters participating in the phenomenon. A relationship enabling reasonably accurate calculation of the diameter of a drop formed by means of such a sphere placed in a stationary or mobile aqueous phase for a wide range of Reynolds numbers and Bond numbers is proposed.

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The efficiency of granular packing coalescence is independent of the nature of the packing for low mass velocities. In the case of packings such as oleophilic resin, ion exchange resins with detergents fixed to them by ionic bonds, or a styrene-divinyl benzene copolymer, this efficiency diminishes and becomes zero for mass velocities greater than the critical velocity. For these velocities, the discharge consists of a dispersion with highly uniform particle size. Study of this has shown that it is generated by the packing and is independent of the input dispersion Even if the experimental conditions of dispersion generation could be described in detail, this would not automatically give an insight into the mechanism of dispersion formation. Among the various possible mechanisms, we consider that which corresponds to drop formation from a continuous film of a dispersed phase surrounding the packing elements as provided by the geometry of the arrangement.

The analogue study leads to a relationship of three dimensionless groups (dg/dS, $\gamma_i/gd_s^2\Delta\rho$, U_fd_s/ν_f) which enable a description of this phenomenon to be made.

Under static conditions, with low values for the dispersed phase flow rate, the proposed relationship enables the diameter of the drops formed from a sphere to be calculated to an accuracy of within 7%.

Under dynamic conditions, the relationship for calculating the drop diameter is established within a wide range of Reynolds number and Bond number variation. The level of accuracy is once again very good.

A wide difference is found between calculated and experimental average size distribution of microdrops emitted by a coalescer; this leads to a rejection of this model for the formation of microdrops in the packing. *This result demonstrates that the microdrops do not arise* from the lamination of a continuous film of a dispersed phase flowing around spherical particles. In addition, this result casts some doubt on the existence of a continuous film which surrounds the materials having a residual hydrophilic character. Parallel studies have shown that hydrophobic packings, for which the condition for the formation of a continuous film is optimal, do not lead to the formation of dispersions in the discharge under the same operating conditions.

The coalescence of secondary dispersions by passage through a porous medium has been known for quite some time. Nevertheless, studies of this process have until now been based only on a system approach, without gaining a deeper understanding of the mechanism of the various stages in experiments, that is, interception of

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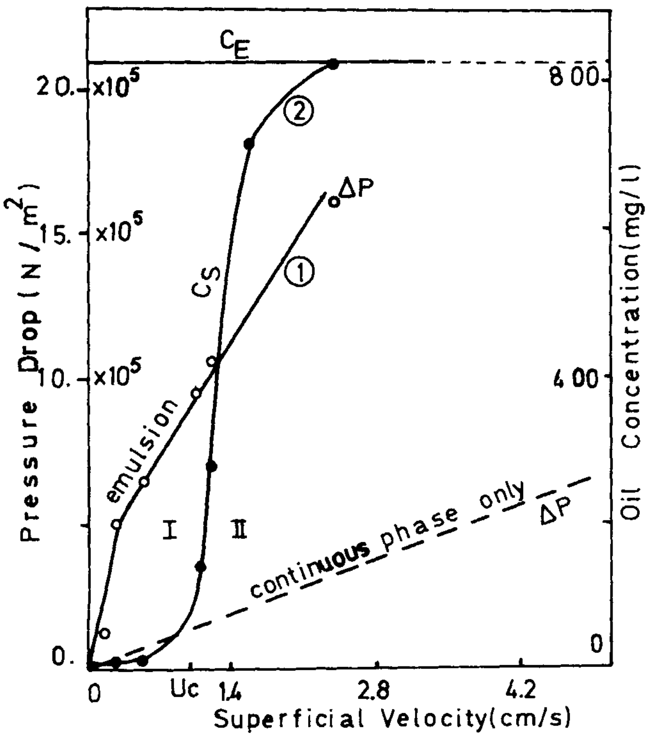

Fig. 1. Influence of superficial velocity on coalescence efficiency.

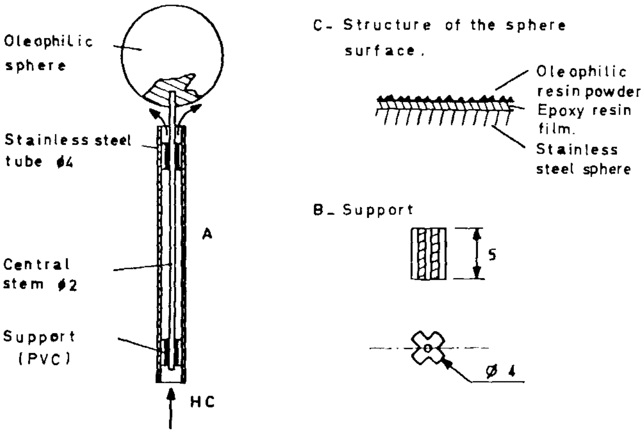

Fig. 2. Apparatus used to study drop formation.

the microdrops within the input dispersion, the retention and circulation of the dispersed phase in the packing, and the emission of the coalesced dispersed phase (Aurelle, 1974; Calteau, 1976).

Under experimental conditions where the initial step is optimized, experience has shown that the overall efficiency can be zero for mass velocities greater than the critical velocity U_c (Calteau, 1976).

Figure 1 shows the result obtained with a packing composed of oleophilic resin beads (Aurelle, 1974) with an average particle size distribution dp of 65 μm, 2 cm high, and placed between two stainless steel grids. The dispersion is formed from the heating oil/water couple ($\gamma_i = 25$ dynes/cm, $\Delta\rho = 0.166$ g/cm^3) containing 1 g/l of heating oil. It is characterized by the following population: ($d_E = 12\ \mu$m, $\sigma = 11\ \mu$m).

The curves (1) and (2) show pressure drop in the packing (ΔP) and the exit concentration (C_s) as a function of U. The curves are plotted when the coalescing régime is reached. The oil concentration is determined by means of catalytic oxidation by carbon dioxide at 900°C using a Precision Scientific Company Precision aquarator. Curve 2 divides the phenomenon into two domaines:

Domaine 1. The dispersed coalesced phase leaves the coalescer in the form of droplets with diameters varying between 0.5 and 2 mm. The effluent is clear and the coalescence efficiency very good.

Domaine 2. The dispersed coalesced phase leaves the coalescer in the form of microdroplets, whose particle size analysis reveals that they form a highly homogeneous population ($d_E = 15\ \mu$m, $\sigma = 4.6\ \mu$m) which is different from that which entered the system. This indicates that an increase in the discharge concentration is not due to a residual fraction of the entering dispersion but rather to a different dispersion generated by the packing. Similar results were observed by Hazlett (1968) during studies on the coalescences of water microdrops dispersed in heating oil.

Among the possible mechanisms, we have considered one corresponding to the formation of microdrops downstream from the particles, this formation arising from a continuous film of a dispersed phase which is laminated by the continuous phase. Such a mechanism has also been suggested by Vinson (1970).

MODEL OF MICRODROP FORMATION WITHIN THE PACKING

Drop formation of one liquid in another nonmiscible liquid has already been the subject of a number of investigations and publications. Studies by Scheele and Meister (1968) deal with the formation of drops leaving a nozzle. The relationship obtained is based on the equilibrium of forces, taking into consideration dispersed phase flow rate and enables drop volume to be calculated to an accuracy of within 11%.

The formation of drops from an orifice defined by adjacent spheres that are nonwetted by the dispersed phase has been examined by Wilkinson (1974). Drop diameter may be determined if the void diameter and the dimensionless group $g\Delta\rho/2\gamma_i$ are known.

The present investigation deals with the formation of drops from a sphere with a low velocity dispersed phase in a stationary or mobile aqueous phase.

It was considered initially with a view to interpreting the formation of microdrops within a coalescer operating beyond its critical mass velocity. It is nevertheless of some significance and originality independent of the coalescence phenomenon, since such an arrangement has to our knowledge never been envisaged.

The study was effected with a large size single sphere model, as shown in Figure 2.

Treatment of the sphere surface with oleophilic resin powder on epoxy resin is designed to give the sphere a certain roughness in order to ensure a good adherence of the hydrocarbon film. The surface was such throughout the study.

The hydrocarbon flow rate within the stainless steel tube is quite low and is maintained constant ($\simeq 0.13$ cm^3/min). This enabled the influence of dynamic forces resulting from the arrival of the hydrocarbon to be ignored (Harkins and Brown, 1919). Figure 3 shows the formation of a hydrocarbon drop when the continuous phase is immobile.

QUANTITATIVE STUDY

Dimensional Analysis

The experiment shows that $dg = f(d_s, U_f, \nu_f, \gamma_i, g\ \Delta\rho)$.

The dimensional analysis of the phenomenon leads to the consideration of three dimensionless groups:

$$I_1 = \frac{d_g}{d_s} \qquad \frac{\text{Drop diameter}}{\text{Sphere diameter}}$$

$$I_2 = \frac{\gamma_i}{g d_s^2 \Delta\rho} \qquad \frac{\text{Interface tension force}}{\text{Force of gravity}}$$

$$I_3 = \frac{U_f d_s}{\nu_f} \qquad \frac{\text{Force of inertia}}{\text{Viscosity force}}$$

Correlation

The ranges of the parameters are given below.

Parameter	Minimum value	Maximum value
U_f(cm/s)	0	18
ν_f(cm^2/s)	0.01	0.35
ds(cm)	0.52	2.23
$g\Delta\rho$(g/cm$^2\cdot$s^2)	45.1	331.6
ν_i(dyne/cm)	4.0	47.0

The experimental study is divided into two parts dealing with static and dynamic regimes.

The value for diameter dg is the arithmetical average of the diameters of five drops formed under the same conditions; the first drop formed previously is not taken into consideration.

The satellite drop volume is assumed to be negligible.

Static study. The aqueous phase is stationary ($U_f = 0$), and the dispersed phase flow rate, which is very low, is maintained constant.

The expression of I_1 as a function of I_2 is deduced from the experimental results summarized in Figure 4. Smoothing of the curve by the least-squares method gives

$$\left[\frac{dg}{ds}\right]_{\text{static}} = 1.63\left[\frac{\gamma_i}{g d_s^2 \Delta\rho}\right]^{0.41} \qquad (1a)$$

FORCE BALANCE

When the continuous phase is stationary and the rate of flow of the dispersed phase is very low, the equivalent diameter of the drop, still attached to the sphere ($dg1$), may be calculated if the rising force (Fas) is considered identical to the bond force (F_c): $Fas = F_c$

$$g \frac{\pi}{6} dg_1^3 \Delta\rho = \pi\, \delta_g \gamma_i$$

where δ_g is the diameter of the circle at the constriction point. This parameter may be determined by photograph. However, where the ratio dg/ds is over 1 (Calteau, 1976), δ_g may be considered the same as ds as an initial approximation.

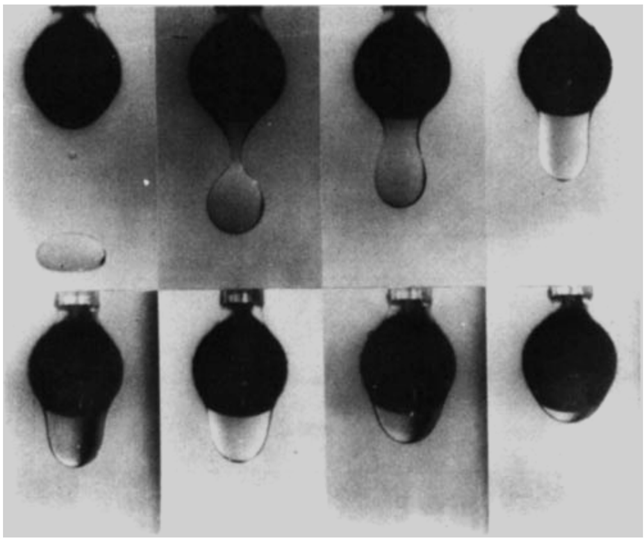

Fig. 3. Photographs of drop formation from a hydrocarbon film flowing around a sphere ($\Delta\rho$ = 0.166 g/cm^3, γ_i = 25 dynes/cm ds = 12.5 mm). The volume of the drop is determined with a microburette with one division corresponding to 0.75 mm^3. During the study, the drop volume was greater than 30 mm^3.

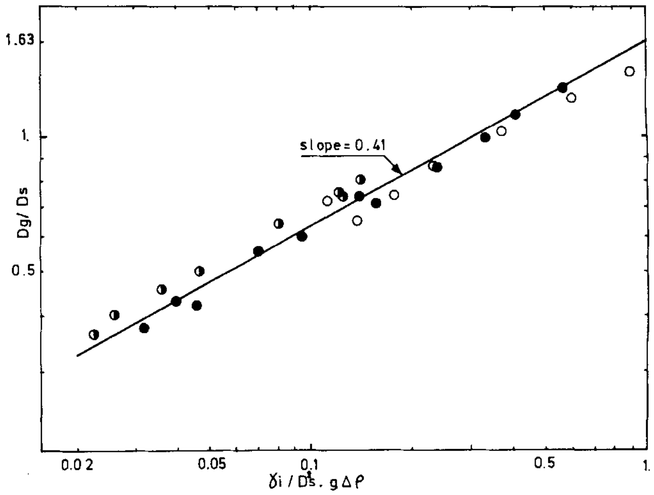

Fig. 4. Empirical correlation of the drop formation phenomenon in a static system.

If on the other hand, for initial calculation purposes, we ignore the volume of the satellite drop that forms in the constriction zone and the small fraction remaining attached to the sphere. The diameter of the drop formed is given by

$$dg_1 = \sqrt{\frac{6\gamma_i\delta_g}{g\Delta\rho}} \qquad (1b)$$

Table 1. Comparison of the Drop Diameter Calculated by Equations (1a) and (1b) at Experimental Values

Dispersed phase	ds, cm	γ_i, dynes/cm	$\Delta\rho$, g/cm^3	$\frac{\gamma_i}{g\,d_s^2\,\Delta\rho}$	δg, cm	dg^*, cm	dg, cm	dg_1, cm	$\frac{dg - dg^*}{dg^*}$	$\frac{dg_1 - dg^*}{dg^*}$
Heating oil	0.52	25.0	0.166	0.568	$\simeq ds$	0.665	0.66	0.77	0.01	0.10
Heating oil	1.82	25.0	0.166	0.046	0.84	0.77	0.84	0.775	0.07	0.01
58% n C_6H_{14} 42% CCl_4	1.02	46.1	0.124	0.344	$\simeq ds$	1.08	1.10	1.34	0.02	0.025
52, 4% n C_6H_{14} 47, 6% CCl_4	1.02	46.1	0.077	0.425	$\simeq ds$	1.28	1.22	1.55	0.06	0.20
Butyl benzoate	0.67	18.0	0.005	8.70	$\simeq ds$	2.46	2.56	2.42	0.04	0.02
Butyl benzoate	1.05	18.0	0.005	3.32	$\simeq ds$	2.86	2.80	2.85	0.02	0.01

Percentage values are by weight. Continuous phase is deionized water.

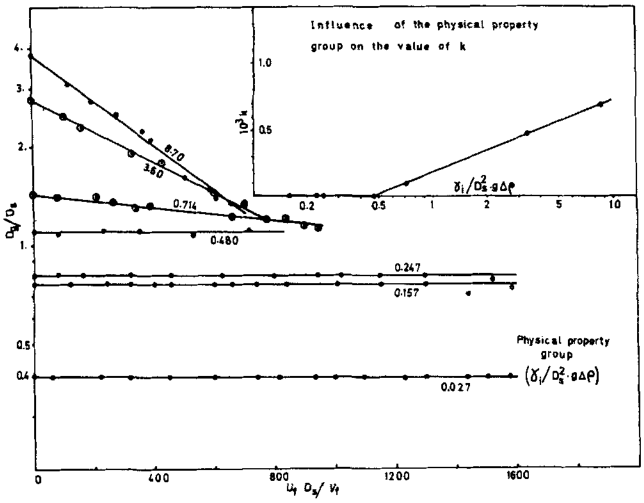

Fig. 5. Empirical correlation of the drop formation phenomenon in a dynamic system.

It is not possible to carry out the correction to take into account the fraction on the sphere by introducing factor F as in Harkins and Brown without previous verification, since the drop is formed here using an arrangement other than a nozzle layout.

Table 1 compares the drop diameters obtained by means of the Calteau relationship (1*a*) (dg) and relationship (1*b*) (dg_1) at the experimental values (dg^*) for different liquid couples and sphere diameters.

At values for group $\gamma_i/gd_s{}^2\Delta\rho$ of from 0.046 to 8.70, the Calteau relationship gives values of dg to an accuracy of within 7%. Relationship (1*b*) gives values that are generally higher than those obtained in the experiment with an error possibly rising to 20%. This is due to the fact that the volume of the drop whose diameter is calculated using (1*b*) comprises the volume of the satellite drop and the fraction remaining on the sphere.

The diameter of the satellite drop is determined by measuring the limit velocity in the continuous stationary phase (Vignes, 1965) and results in a value of 1.1 mm for a drop of 7.5 mm. The ratio of the volume of the satellite drop to that of the main drop is of the order of 0.003, which means that we are therefore justified in ignoring the satellite drop volume.

Dispersed phase	Continuous phase	U_f, cm/s	d_p, cm	$(d_E/d_p)_c$	$(d_E/d_p)_e$
Heating oil	Water	24	65×10^{-4}	57.5	0.23
Butyl benzoate	Water	36	65×10^{-4}	146	0.32
Cyclohexane	Water	48	65×10^{-4}	46.5	0.30

Dynamic Study ($I_3 \neq 0$)

The dispersed phase flow rate is maintained constant, and the continuous phase flows around the sphere at velocity U_f.

A rigorous analytical study of drop formation with the aqueous phase in motion should take into account the following parameters: drag due to viscosity and pressure due to flow, the resultant of gravity and Archimedes thrust, interfacial tension force, and dynamic force due to dispersed phase input.

Though such a study would be very fruitful, it would be highly complicated, and this is one of the reasons we have undertaken a dimensional examination of the phenomenon and established correlation functions following experimental work.

On Figure 5 are plotted a series of curves representing I_1 as a function of I_3 for several values of I_2. The conclusions obtained are as follows: for $I_2 < 0.48$ the ratio dg/ds is less than 1 and is not affected by the variation of I_3, for $I_2 > 0.48$ the ratio dg/ds diminishes when I_3 increases. For $I_3 > 800$, another drop formation pattern appears which is not studied here. In this case, the drops are emitted by a digitation subjected to turbulence due to the preponderance of inertial forces.

Smoothing of the curves leads to a correlation of the following form:

$$\left\{\begin{array}{ll} (I_1)_{\text{dynamic}} = (I_1)_{\text{static}} \cdot 10^{-kI_3} & \\ k = 0 \quad \ldots\ldots\ldots\ldots & \text{for } \; I_2 < 0.48 \\ k = 0.545 \times 10^{-3} \log I_2 & \text{for } \; I_2 > 0.48 \end{array}\right. \tag{2}$$

If I_1, I_2, and I_3 are replaced by their equivalent forms, we obtain

$$\left\{\begin{array}{ll} \dfrac{dg}{ds} = 1.63 \left[\dfrac{\gamma_i}{gds^2\Delta\rho}\right]^{0.41} \times 10^{-k\frac{U_f ds}{\nu_f}} & \\ k = 0 \quad \ldots\ldots\ldots\ldots & \text{for } \; \dfrac{\gamma_i}{gds^2\Delta\rho} < 0.48 \\ k = 0.545 \times 10^{-3} \log\left[\dfrac{\gamma_i}{gds^2\Delta\rho}\right] & \text{for } \; \dfrac{\gamma_i}{gds^2\Delta\rho} > 0.48 \end{array}\right. \tag{3}$$

The diagram shown in Figure 5 gives the areas of validity of the semiempirical relationship (3) while indicating those areas to be examined in further possible studies.

CONCLUSION

A bed of spheres with an average particle size distribution of dp generates microdrops having an average size distribution of d_E. If it is assumed that they are generated from a continuous film, the application of relationship (3) yields the values $(d_E/dp)_c$ which are clearly greater than those experimentally obtained $(d_E/d_p)_e$ given the intersticial velocity within the packing.

Such a microdrop formation mechanism within the bed is thus highly improbable. This result renders doubtful the existence of a continuous film of a dispersed phase around the particles. The microscopic observation of the phenomenon on a transparent model demonstrates the existence of agglomerates of a dispersed phase which are locally present on packings such as divinyl benzene copolymer of oleophilic resins. These agglomerates of the dispersed phase act as centers which generate the microdrops appearing in the effluent beyond the critical velocity (Calteau, 1970). This study has moreover provided a means of establishing a relationship enabling reasonably accurate calculation of the diameter of a drop formed by means of a sphere placed in a mobile aqueous phase for a wide range of Reynolds number and Bond number variations.

NOTATION

C_E = concentration at coalescer input
C_s = concentration at coalescer output
dg^* = experimental value of the diameter of the drop formed as defined by equation (1a)
d_g = diameter of the drop formed
dg_1 = diameter of the drop still attached to the sphere
d_p = diameter of packing element
d_E = average microdrop size
g = gravitational acceleration
U = mass velocity (dispersion flow rate/column section)
U_c = critical velocity
U_f = water velocity

Greek Letters

δ = diameter of the circle at the constriction point as defined by Equation (1b)
γ_i = interface tension
$\Delta\rho$ = density difference between the two phases
Δp = pressure difference at the poles of the coalescer
σ = standard deviation
ν_f = kinematic viscosity of continuous phase

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Vapor-Liquid Equilibrium Measurements Through Vapor-Adsorption Chromatography

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Further understanding of the application of perturbation chromatography as applied to gas-adsorption systems enables one to study vapor-liquid equilibria at finite concentrations. The generalized relations for the determination of gas adsorption on arbitrary adsorbents using the principles of perturbation chromatography were developed by Gilmer and Kobayashi (1965). Perturbation chromatography has been successfully applied to study the adsorption of gas mixtures on several adsorbents (Gilmer and Kobayashi, 1964; Haydel and Kobayashi, 1967; Masukawa and Kobayashi, 1969).

Adsorption chromatography was used by Masukawa et al. (1968) to show that the dew point could be viewed as a limiting condition of gas adsorption. They introduced the hypothetical perfect gas perturbation to obtained adsorbed phase properties (Masukawa and Kobayashi, 1968*a*). They also showed that the condensed state could be defined within very narrow limits, that is, tens of Angstrom units. Kobayashi and Carnahan (1975) defined the dew point in explicit Gibbsian terms and used the earlier measurements of Masukawa and Kobayashi (1968*b*) as an example of the mixture dew point definition.

Through careful selection of a homogeneous adsorbent for a given type of adsorbate, Porapak P, for the methane-*n*-butane system, the authors have found that the *K* value for adsorbent, defined by

$$K_i = \frac{y_i}{x_i} \tag{1}$$

where y_i is the mole fraction of component *i* in the elution gas phase, and x_i is the mole fraction of the adsorbate in the adsorbed phase, is essentially independent of the pressure, Figure 1. From the determination of the *K* value for the components in a mixture by methods described earlier (Masukawa and Kobayashi, 1969), from determination of the very onset of condensation from the detector signal, Figure 2, and from the behavior of the adsorption isotherm, Figure 3, it has been found possible to determine the vapor-liquid equilibrium constants for the components in the mixture (Everett, 1977). Similar results were obtained at 255.37° and 244.26°K (0° and −20°F) for the methane-3 mole % *n*-butane mixtures and for a methane-5 mole % *n*-butane mixture at 266.48°, 255.37°, and 244.26°K (+20°, 0°, and −20°F). The V-L-E *K* values determined by classical methods at 255.37°K (−20°F) are also shown on Figure 1 and found to agree quite satisfactorily with the V-L-E *K* values determined by adsorption chromatography.

A precise method for determining vapor-liquid equilibria as a limiting case of gas-adsorption chromatography is presented. The small, radioactive samples were injected into the flowing system in the gaseous state with a six-port injection and column bypass switching valves (model CV-H Pax from the Valco Instruments Co., Houston, Texas) with special rotors for low temperature work. If

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