NOTE

RAPID DETERMINATION OF SUSPENDED SOLIDS IN WATERS BY FLOTATION

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Suspended solids at the mg/l levels in fresh and waste waters are coagulated by stirring with cetyldimethylbenzylammonium chloride and sodium chloride, and quantitatively floated to the solution surface within 30 s with numerous tiny bubbles. This technique is more rapid than filtration with 0.45- μ m membrane filters.

Suspended solids (SS) make water turbid, adsorb or incorporate some toxic trace substances, and have bad influences upon the use of water. Therefore the determination of total amounts of SS is necessary for the evaluation of water quality. At present, it seems reasonable to define SS as the remaining fraction on a 0.45- μ m membrane filter, because this definition is conventionally accepted in geochemistry and practically turbidity is completely removed by this filter. Filtration with this filter, however, is often difficult or impossible due to clogging. Filtration with No.6 paper filters¹⁾ (3- μ m nominal porosity) is rapid, but the filtrate is still turbid. Centrifugation is not applicable to the separation of SS having densities near unity, and it is not convenient for large sample volumes.

Although Grieves et al.²⁾³⁾ proposed a flotation technique for clarifying turbid waters, we found that tiny SS were not quantitatively floated by their technique. This can be ascribed to the direct flotation of SS with larger bubbles. In the present work, SS are coagulated to 0.5 - 2 mm, and then floated by tiny bubbles of 0.1 - 0.5 mm in diameter. This improved technique is suitable for rapid and quantitative separations of SS and successfully applied to fresh and industrial waste waters.

EXPERIMENTAL

Apparatus. A flotation cell and a sampling vessel, both made of Pyrex glass, are shown in Fig. 1. The detachable polyethylene insert⁴⁾ prevents adhesion of a scum on the walls of the flotation cell near the solution surface. A Shimadzu model UV-180 spectrophotometer with matched 1-cm cells was used for turbidimetry.

Reagents. Kaolin and bentonite (particle size: 1 - 10 μ m, Nakarai Chemicals) were used; the water-soluble fraction was less than 1 %. Cationic surfactants (Tokyo Kasei Kogyo, Extra Pure Reagents) or anionic surfactants (Nakarai Chemicals, Extra Pure Reagents) were dissolved in 70 % ethanol (1 mg/ml).

Recommended procedure. To a 500-ml sample solution in a 500-ml beaker, add 2 ml of sodium chloride solution (50 mg/ml) and 3 ml of cetyldimethylbenzylammonium chloride (cationic surfactant) solution, and stir the solution for 5 min by

Fig. 1 Glass flotation cell and sampling vessel

a magnetic stirrer with a 50-mm stirring bar at 500 rpm. Transfer the solution quantitatively to the flotation cell, and place the polyethylene insert near the solution surface. Pass nitrogen at a flow-rate of $1 - 1.5 \text{ ml cm}^{-2} \text{ min}^{-1}$ from the lower end of the flotation cell for 15 - 30 s to effect complete flotation of SS. Suck the resulting scum-foam mixture on the solution surface into the sampling vessel with the stopcock open (see Fig. 1). Take out the polyethylene insert from the flotation cell, and transfer the adhering scum into the sampling vessel by spraying 0.5 - 1 ml of water. Close the stopcock, and suck off the solution. Disassemble the upper compartment of the sampling vessel, and place the membrane filter together with the glass cylinder on a watch glass. Dry at $105 - 110^\circ \text{C}$ for 1 hr, cool in a desiccator, and then weigh; check the weight constancy ($\pm 0.5 \text{ mg}$). Obtain the weight of the SS by subtracting the weight of the cylinder, filter and watch glass.

Turbidimetry. Recoveries (%) of SS were also estimated from $100(A_1 - A_2)/A_1$, where A_1 and A_2 are the absorbance at 400 nm of the solution before and after the flotation.

RESULTS AND DISCUSSION

The flotation process was examined by using suspensions of kaolin and bentonite. Since clay particles are negatively charged in water⁵⁾, they can be converted into hydrophobic and floatable with cationic surfactants. Under similar conditions to those of Grieves et al.^{2,3)}, 10 - 15 ml of aqueous cetyldimethylbenzylammonium chloride solution (1 mg/ml) was added to 500 ml of water containing

40 mg each of kaolin and bentonite, and nitrogen was passed at a flow-rate of 50 ml $\text{cm}^{-2} \text{min}^{-1}$ for 10 min through a No.2-sintered glass disk (40- to 50- μm nominal porosity). Bubbles of 1 - 5 mm in diameter rose rapidly and a copious foam layer was produced on the solution surface, leaving appreciable amounts of clay particles in the solution. Even if the flotation was repeated once more, the clay recoveries were 50 - 70 % (by turbidimetry).

Therefore, we tried an improved flotation technique described in the Recommended procedure. Clay particles were coagulated to 0.5 - 2 mm before the flotation by stirring with cetyldimethylbenzylammonium chloride and sodium chloride (for increasing ionic strength). Numerous tiny bubbles (0.1 - 0.5 mm diam.) were generated by a No.4-sintered glass disk (5- to 10- μm nominal porosity) in the presence of small amounts of ethanol⁶⁾. The clay flocs were easily floated by capturing bubbles on the surfaces and in the interstitial spaces of the flocs, and a stable scum mixed with a relatively small amount of foam was formed on the surface of the solution within 30 s.

Kaolin and bentonite, 40 mg each, in 500 ml of water were recovered in greater than 95 % yields (by turbidimetry) over the pH range 3 - 9, with 2 - 5 ml of cetyldimethylbenzylammonium chloride solution, 1 - 4 ml of sodium chloride solution, and 2 - 10 min of stirring. Flotation with other cationic surfactants was also examined, but a little lower recoveries were obtained: 81 and 90 % with cetylethyl-dimethylammonium bromide, and 87 and 87 % with cetyltrimethylammonium bromide. With anionic surfactants, sodium oleate, sodium dodecyl sulfate or sodium dodecyl-benzenesulfonate, clay particles were not floated.

Table 1 shows that various quantities of clay and river sediment particles are quantitatively separated by the recommended procedure. Because the sample solution collected together with the scum was only ca. 2 ml, the removal of the solution by

Table 1 Flotation of clay and river sediment particles
in 500 ml of water

Added (mg)	Recovery (%) measured by	
	weighing	turbidimetry
1:1 Mixture of kaolin and bentonite (dispersed by magnetic stirring, particle size 1 - 10 μm)	20	95
	30	97
	40	98
	60	95
	80	99
	100	97
River sediment (dispersed by ultrasound, particle size 1 - 10 μm)	7.5	98
	15	100
	30	100
	45	100
	60	100

suction filtration was rapid. The surfactant accompanying the particles was determined as follows. The floated particles were collected in the sampling vessel by the recommended procedure, and transferred together with the filter into a 30-ml beaker with 5 ml of ethanol. The surfactant was completely desorbed from the particles by irradiating ultrasound (29 kHz, 40 W) for 3 min, and the filter and particles were removed by centrifugation at 15,000 rpm for 10 min. The surfactant in the supernatant solution was titrated with a standard sodium dodecylbenzene-sulfonate solution (Toluidine Blue as indicator)⁷⁾, and found to be less than 1 mg. Metal ions, colloidal hydrated metal oxides passing through a 0.45- μ m filter, and dissolved humic acid are not floated at all.

Table 2 shows that the same values as those with 0.45- μ m filters are rapidly obtained by the recommended procedure. When the SS in the waste water were separated with a 5- μ m membrane filter after coagulation by stirring with cetyldimethylbenzylammonium chloride and sodium chloride, the filtration required ca. 2 hr.

Table 2 Determination of SS in water samples

Sample (500 ml)		Flotation	Suction filtration with	
			Membrane filter (Millipore HA, 0.45 μ m, 47 mm diam.)	Paper filter (Toyo Roshi No.6, 3 μ m, 55 mm diam.)
Pond water	SS (mg/l)	78	75	31
	Time* (min)	15	45	20
Waste water from a starch factory	SS (mg/l)	74, 78	79	50
	Time*	20, 20	280**	70

* required for separation only.

** 5 sheets renewed during the filtration.

The application of the present technique to the determination of trace heavy metals associated with SS in fresh waters will be published elsewhere.

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