barium titanate single crystals are more rectangular than those from ceramics. Of importance for telephone switching applications also is the fact that, at least in specially prepared single crystals, the coercive force, *i.e.*, the field required to reverse the polarization, is much lower than in ceramics.

Barium titanate crystals have been grown by several different methods but we have not observed in any of them the desired rectangular hysteresis loops at sufficiently low fields. This includes crystals grown from $BaCl_2$ solutions by the method of Blattner, Matthias, Merz and Scherrer,[3] by the flame fusion method and from the pure melt by the Stockbarger process.

We have developed a method of preparing barium titanate crystals which yields large, clear single crystals having the desired ferroelectric characteristics. Furthermore these crystals are obtained in the form of thin plates which lend themselves readily to storage device applications.

A typical procedure by which it has been possible to grow good single crystals of barium titanate is to start with a mixture containing approximately 30% of barium titanate (C.P.), 0.2% of ferric oxide (Reagent) and the balance of potassium fluoride (C.P. Anhydrous). The barium titanate and ferric oxide are placed in a platinum crucible (standard low form) and then covered with the potassium fluoride. The crucible containing this charge is covered with a platinum lid and placed directly into a furnace which is at a temperature between 1150 and 1200°. The furnace is held at this temperature for eight hours and then cooled at a slow constant rate until a temperature of 850 to 900° is reached. The still liquid flux is poured off at this point and the crystals are annealed by slowly cooling down to room temperature. This particular procedure is one adapted to our equipment and may of course be varied. The important considerations are (1) to get a considerable quantity of barium titanate in solution, (2) to allow crystallization to take place slowly enough to minimize unwanted nucleation, but fast enough to preserve the plate habit, and (3) to anneal the crystals by slow cooling in an unstrained condition.

Two different habits of crystal growth are observed in these experiments. A mass of chunky crystals is usually found on the bottom of the crucible. Growing out of this layer are numbers of thin plates, always in pairs, which for lack of a better name are called butterfly wings. These extend upwards into the melt. The crystal plates may be separated from the flux by soaking the crucibles in hot water which dissolves the fluoride rapidly. The thin plates produced in this way have been found to be more perfect and approximate more nearly to "single domain" crystals than any others which have come to our attention. By this is meant that thin, large area crystals are obtained which are relatively free from so called 90° walls and in which the polar direction (*c*-axis) is usually perpendicular to the major crystal faces. This is important for obtaining the desired rectangular hysteresis loops and low coercive force. Some of the characteristics of these barium titanate single crystals have been described by Merz.[4]

Many of the early barium titanate crystals were found to be dark colored and to have too high a conductivity for storage circuit applications. This might be traceable either to impurities or to a loss of oxygen during the crystal growing process. We have found that crystals with much lower dielectric loss are obtained if a small amount of Fe_2O_3 is added to the melt from which they are grown. Measurements were made by Mr. F. J. Morin of these laboratories of the sign of the thermoelectric effect in barium titanate crystals containing various amounts of added iron. It was observed that crystals grown in potassium fluoride without added Fe_2O_3 were *n*-type semiconductors at elevated temperatures. This may be the result of the loss of oxygen resulting in donor ions being produced. The addition of Fe_2O_3 supplies acceptor ions and if the number of these is just such as to compensate for the donors the crystals become intrinsic semiconductors. A minimum of conductivity and a change of sign of the thermoelectric effect are observed at about 0.2 atomic percentage of added iron. The amount of iron required for this compensation depends upon the conditions of growing the crystal, *i.e.*, upon the presence of other impurities and the amount of loss of oxygen. The latter in turn depends upon the temperature of crystallization and the time that the melt was held at high temperatures. It is observed also that the iron lowers the Curie temperature very markedly. Crystals containing 0.2% iron have a Curie temperature of about 105 to 110° while those containing 2.5 atomic percentage of added iron are cubic at room temperature. X-Ray studies by Mrs. E. A. Wood have shown that the *c*/*a* ratio decreases with added iron.

This procedure for growing barium titanate crystals has been useful for producing crystals for experimental purposes. The choice of potassium fluoride as a solvent is a good one from the standpoint of solubility of barium titanate. However, it should be pointed out that it reacts readily with the furnace refractories so that their life is short. The usual precautions in handling fluorides should be observed and such work should, of course, be done only in a well ventilated space.

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Low Concentration Chemistry. VII. Investigations on the Role of Adsorption in Radiocolloid Formation

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Radiocolloid formation has been attributed by some investigators to an adsorption of cations in very low concentrations upon negatively charged impurities in basic solutions, thus simulating true colloids.[1] If this adsorption of ions upon impurities is a factor of primary importance in radiocolloid formation, then it should be possible to assume that anions in low concentrations would behave accordingly and be adsorbed upon positively charged impurities in acid solutions, thus also simulating colloids. Also, if adsorption is an important factor cations which do not form insoluble hydroxides should show radiocolloidal behavior as well as those which do. The purpose of these experiments was to test the assumption that the primary factor in

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(3) Blattner, Matthias, Merz and Scherrer, *Helv. Chim. Acta*, **30**, 225 (1947); *Experientia*, **3**, 4 (1947).

(4) W. J. Merz, *Phys. Rev.*, **91**, 513 (1953).

(1) G. K. Schweitzer and M. Jackson, *J. Chem. Education*, **29**, 513 (1952).

radiocolloid formation is an adsorption phenomenon. The materials used were calcium-45, sodium-22, cesium-134, sulfur-35-labeled sulfate, iodine-131-labeled iodide and phosphorus-32-labeled phosphate.

Experimental

Materials.—All inactive chemicals were of analytical reagent quality. All radioactive nuclides were obtained from the Oak Ridge National Laboratory. Ordinary distilled water was used in preparation of solutions.

Cations.—Sodium-22 was obtained as sodium chloride in dilute hydrochloric acid. The nuclide has a half-life of 2.6 years, decaying to stable neon-22 by emission of a 0.58 Mev. positron plus a 1.28 Mev. gamma.[2] Calculations based on the stated specific activity indicated that the sodium concentration of the experimental solutions was about 10^{-4} *M*.

Cesium-134 was received as cesium chloride in dilute hydrochloric acid. The nuclide has a half-life of 2.3 years, decaying to stable barium-134 by emission of 0.090 and 0.658 Mev. betas plus gammas.[2] Calculations based on the stated specific activity indicated that the cesium concentration of the experimental solutions was about 10^{-7} *M*.

Carrier-free calcium-45 with a half-life of 152 days, which decays to stable scandium-45 by emission of a 0.254 Mev. beta,[2] was obtained as calcium chloride in dilute hydrochloric acid. No available test was positive for calcium, and hence the concentration was estimated to be 10^{-7} *M* or less.

Anions.—Iodine-131 was obtained as sodium iodide in a dilute sodium hydrogen sulfite solution at a *p*H of 11.0. The nuclide has a half-life of 8 days, decaying to stable xenon-131 by emission of 0.33, 0.60, 0.15 and 0.81 Mev. betas plus gammas.[2] The shipment also contained 0.9% iodine-131. Employing the microchemical test as given by Steigmann[3] the concentration of iodide in the experimental solutions was calculated to be approximately 10^{-7} *M*.

Sulfur-35 was obtained as the carrier-free sulfate in dilute hydrochloric acid. The nuclide has a half-life of 87.1 days, decaying by emission of a 0.166 Mev. beta to stable chlorine-35.[2] No indication of the presence of sulfate could be obtained using the microchemical test for sulfate given by Feigl[4] or by addition of barium chloride. Calculations based upon the solubility of barium sulfate indicated that the sulfate concentration must have been 10^{-8} *M* or less.

Phosphorus-32 was obtained as the phosphate in dilute hydrochloric acid. The nuclide has a half-life of 14.30 days, decaying to stable sulfur-32 by emission of a 1.712 Mev. beta.[2] No indication of the presence of phosphate could be obtained using the sensitive microchemical test given by Feigl.[4] Allowing for dilution this should place the maximum phosphate concentration of the experimental solutions at less than 10^{-7} *M*.

Preparation of Solutions.—Initial separations were unnecessary. Upon arrival the shipments of calcium-45, sodium-22 and cesium-134 were immediately transferred to polyethylene bottles. Contact with glass was avoided during preparation of solutions by use of paraffined containers. Glass bottles were used for iodine-131, sulfur-35 and phosphorus-32. As required in the experiments portions of the shipments were taken and diluted with 0.01 *N* hydrochloric acid. Samples containing calcium, sulfate, iodide or phosphate were adjusted to the desired *p*H values by adding either sodium hydroxide or hydrochloric acid solution. Those containing sodium or cesium were adjusted to the desired *p*H by adding ammonium hydroxide or hydrochloric acid solution. Measurement of *p*H was made using a Beckman Model G-2 Glass Electrode *p*H Meter and microelectrodes.

Sample Preparation.—Samples for counting were taken with a 0.100-ml. micropipet and syringe. These samples were placed on copper planchets or glass cups and evaporated to dryness with an infrared lamp. Glass cups were used only when the solution being sampled was strongly acidic or basic.

Radioactivity Apparatus.—All radioactivity measurements were made with a 1.4 mg./cm.^{2} Nuclear D-34 Mica End-window Geiger Tube connected to a Nuclear Model 163 Scaler. All samples were counted for a sufficiently long time to give a standard deviation equal to or less than 1%.

Filtration.—Ten-ml. portions of the radioactive solutions initially 0.01 *N* in hydrochloric acid were adjusted to desired *p*H values and divided into two 5-ml. portions which were filtered through Whatman No. 50 filter paper. Each filter paper had been soaked with an inactive solution of identical salt concentration and *p*H prior to filtration of the active sample. Samples were taken before and after filtration, the differences in radioactivities being used to determine the percentage removal.

Centrifugation.—Portions of the radioactive solutions initially 0.01 *N* in hydrochloric acid were adjusted to the desired *p*H values and placed in centrifuge tubes holding about 0.6 ml. Plexiglas tubes were used for calcium, sodium and cesium and glass tubes for sulfate, iodide and phosphate. After sampling, the solutions were centrifuged for 30 minutes in a Misco Electric Micro Centrifuge at about 25,000 times gravity, and then resampled. The differences in radioactivities were again employed as a measure of the percentage removal. Corrections were applied for adsorption onto the plexiglas or glass tubes.

Adsorption.—Samples of dry 140 mesh clay and Norit "A" carbon of 0.200 g. each were weighed out into 15-ml. ground glass weighing bottles and three glass beads added. Following adjustment of *p*H and sampling, each active solution was divided into two 5-ml. portions which were added to the weighing bottles containing clay or carbon. The contents were shaken for an hour by a mechanical shaker, the clay or carbon removed with a low speed centrifuge, and each solution again sampled. The adsorption upon weighing bottles and glass beads was determined and taken into account in determining the percentage removal from the differences in radioactivities. The *p*H of all samples was again measured at the end of the experiment and the results were taken as the final equilibrium *p*H values.

Results

Sodium.—Filtration of two samples of sodium, at each *p*H value from 0 to 10, resulted in an erratic removal of from 7 to 14%. Simultaneously with filtration studies, two samples of sodium, at each *p*H value from 0 to 10, were centrifuged. This resulted in an erratic removal of from 0 to 2% which is within the error of the method. The removal by filtration could thus be attributed to adsorption on the filter paper.

Cesium.—Filtration of two samples of cesium, at each *p*H value from 0 to 10, resulted in an erratic removal of from 9 to 17%. Simultaneously with filtration studies two samples of cesium, at each *p*H value from 0 to 10, were centrifuged. This resulted in an erratic removal of from 0 to 2%. The majority of the samples showed no removal at all by centrifugation, thus the slight removal by filtration could be attributed to adsorption on the filter paper. A portion of the determinations were carried out intentionally under extremely bad dust conditions.

Calcium.—The results of centrifuging samples of calcium are represented by Fig. 1. All values are averages of at least three separate determinations with the average deviation shown by a vertical line if it is 3% or greater. Only limited filtration studies were made. Using a fine glass frit 27% was removed at a *p*H of 7, but in the *p*H range of 9 to 13 from 97 to 100% was removed. Filtration of samples through Whatman No. 50 filter paper at *p*H values of 10 and 12 resulted in a removal of 66 and 69% of the activity, respectively. The greater removal by the glass frit could be due to ion exchange which would not occur with the filter paper. Adsorption probably was involved in both the glass frit and filter paper experiments.

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[2] Oak Ridge National Laboratory, "Isotopes," Carbide and Carbon Chemical Company, Oak Ridge, 1952.

[3] A. Steigmann, *J. Soc. Chem. Ind.*, **61**, 82 (1942).

[4] F. Feigl, "Laboratory Manual of Spot Tests," Academic Press, Inc., New York, N. Y., 1943.

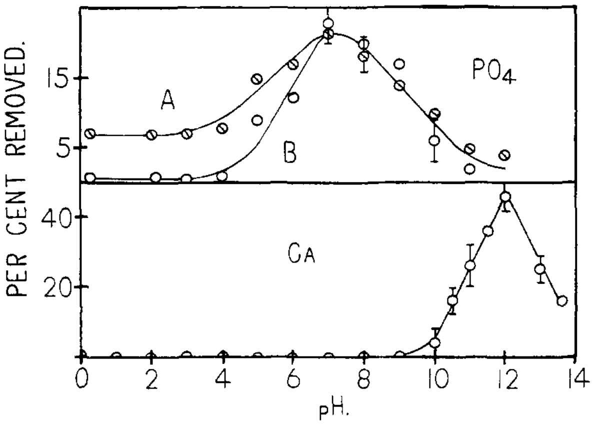

Fig. 1.—Lower graph, percentage of calcium removed by centrifugation from tracer solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H; upper graph, percentage of phosphate removed by filtration (A) and centrifugation (B) from tracer phosphate solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H.

Iodine.—Filtration of four samples of iodide, at each *p*H value from 1 to 12, resulted in a very erratic removal of from 11 to 30%. Simultaneously with the filtration studies, four samples were centrifuged at each *p*H value from 2 to 12, resulting in an erratic removal of from 0 to 3%. Adsorption studies of iodide on clay and carbon also were carried out. Curve A of Fig. 2 represents adsorption of iodine-131 on clay as the *p*H is varied. Likewise curve B represents adsorption of iodine-131 on Norit "A" carbon. Each point represents a single determination with exception of a few which were identical. The final equilibrium *p*H is shown.

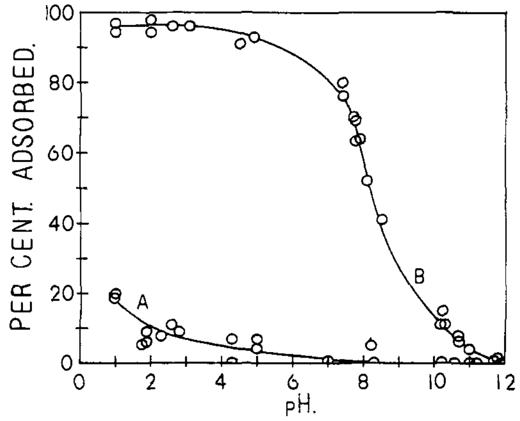

Fig. 2.—Percentage of iodide adsorbed onto clay (A) and Norit A carbon (B) from tracer iodide solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H.

Sulfate.—Centrifugation of two samples of sulfur-35-labeled sulfate at each *p*H value from 0.5 to 12, resulted in no removal at any *p*H. Filtration of two samples of sulfate, at alternate *p*H values from 2 to 10, resulted in an erratic removal of from 6 to 10% which could be attributed to adsorption on the filter paper. Also adsorption studies of sulfate on clay and carbon were carried out. Curve A of Fig. 3 represents adsorption on clay. Likewise curve B represents adsorption on Norit "A" carbon. Each point represents a single determination. The final equilibrium *p*H is shown.

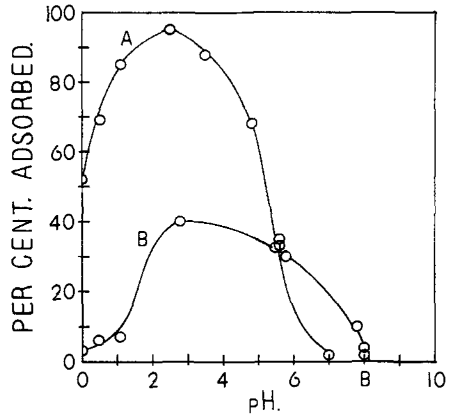

Fig. 3.—Percentage of sulfate adsorbed onto clay (A) and Norit A carbon (B) from tracer sulfate solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H.

Phosphate.—The results obtained from filtering samples of phosphorus-23-labeled phosphate as the *p*H was varied are represented by curve A of Fig. 1. Each point represents the average of two determinations. Likewise, curve B represents the results of centrifuging at least three samples of each *p*H value. The average deviation if 3% or greater is represented by a vertical line. Adsorption studies of phosphate on clay or carbon are shown in Fig. 4. Curve A represents adsorption on clay while curve B represents adsorption on Norit "A" carbon. Each point represents a single determination except for a few identical results. The final equilibrium *p*H is shown.

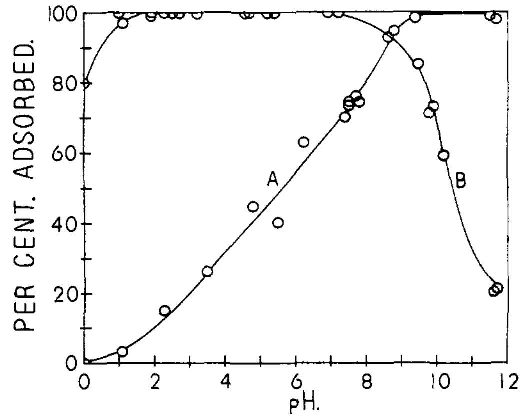

Fig. 4.—Percentage of phosphate adsorbed onto Norit A carbon (A) and clay (B) from tracer phosphate solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H.

Conclusions.—Under the conditions of these experiments sodium, cesium, sulfate and iodide showed no definite evidence of radiocolloidal formation. Calcium and phosphate showed some type of aggregation under certain conditions which allowed some removal. However, in neither case did the removal exceed 50% nor were the curves similar to those of elements previously reported to be radiocolloidal.[1]

The adsorption curves of iodide, sulfate and phosphate on clay or carbon were not at all similar to removal curves obtained by filtration or centrifugation. On the basis of this evidence and the failure of soluble cations to show definite radiocolloidal properties, it is concluded that adsorption of ions upon impurities does not appear to be the primary factor in radiocolloid formation.

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Fluoroölefins. III. 1,1-Difluorobutadiene and 1-Fluoro-1-chlorobutadiene[1]

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Although 1,1,1-trichloroethane reacts readily with hydrogen fluoride to give corresponding fluorine substituted products,[2] practically no information is available about the fluorination of similar compounds in the butane group. One reason for this lack of information has been the difficulty in obtaining compounds having the trichloromethyl group; however, this situation has now been improved due to the discovery by Kharasch[3] that bromotrichloromethane reacts readily with terminal olefins to give good yields of 1,1,1-trichloro-3-bromoalkanes. Because of the availability of 1,1,1,4-tetrachloro-3-bromobutane, obtained by the reaction of bromotrichloromethane with allyl chloride, and because the fluorinated derivatives should lead to olefins and dienes of interest, a study was made of its fluorination.

TABLE I

FLUORO COMPOUNDS OBTAINED FROM 3-BROMO-1,1,1,4-TETRACHLOROBUTANE

Compound	B.p., °C.	P, mm.	T, °C.	n_D	d_4	MRD Calcd.	MRD Found	Ag eq.[a] Calcd.	Ag eq.[a] Found	Chlorine, % Calcd.	Chlorine, % Found
$CFCl_2CH_2CHBrCH_2Cl$	77.4	10	26	1.4916	1.784	42.9	41.8	64.6	65.1		
$CF_2ClCH_2CHBrCH_2Cl$	52.4	10	25	1.4551	1.731	37.97	37.93	80.3	80.0		
$CF_2ClCH_2CHFCH_2Cl$	118.4–118.5	760	27	1.3881	1.428	30.12	30.17	[b]			
$CF_3CH_2CHBrCH_2Cl$	135.0–135.5	760	25	1.4156	1.698	32.92	33.10	112.3	114.9		
$CFCl_2CH_2CH{=}CH_2$	88.0	760	27	1.4104	1.188	29.85	30.00			49.6	49.6
$CF_2ClCH_2CH{=}CH_2$	49.2	760	25	1.3550	1.103	24.88	24.95			2.08	28.3
$CFCl{=}CHCH{=}CH_2$	53.4	760	25	1.4267	1.066	24.51	25.50			33.4	33.8
$CF_2{=}CHCH{=}CH_2$	3.5–4.0	760									

[a] Silver equivalent which is defined as the molecular weight divided by the number of halogen atoms other than fluorine. [b] *Anal.* Calcd. for $C_4H_5F_3Cl_2$: C, 26.57; H, 3.18. Found: C, 26.71; H, 2.83. [c] *Anal.* Calcd. for $C_4H_4F_2$: mol. wt., 90.1. Found: mol. wt., 91.5.

In an effort to effect replacement of the chlorine atoms of the trichloromethyl group, an investigation was made of the effectiveness of several of the more commonly used fluorinating agents such as antimony trifluoride or antimony trifluorodichloride, and hydrogen fluoride alone and with mercuric oxide.

Of the reagents studied, only the combination of antimony trifluoride and trifluorodichloride was found to give satisfactory results and even in this case variations in the conditions employed exerted a pronounced effect upon the relative amounts of the fluorobutanes. In one run, in which antimony trifluoride (1.7 moles) and antimony trifluorodichloride (1.3 moles) were allowed to react with 1,1,1,4-tetrachloro-3-bromobutane at 40–50°, a 51% yield of 1,1-difluoro-1,4-dichloro-3-bromobutane was obtained. When the reaction was carried out at a higher temperature or by using a larger proportion of antimony pentahalide, the amount of 1,1-difluoro compound was decreased and more highly fluorinated material was obtained. For example, at 60° and using antimony trifluoride (0.4 mole) and antimony trifluorodichloride (0.6 mole) only a 17% yield of 1,1-difluoro-1,4-dichloro-3-bromobutane was obtained but 1,1,3-trifluoro-1,4-dichlorobutane was separated in a 20% yield. The properties of the various derivatives which were obtained are given in Table I.

The substitution reaction proceeded normally to give the various products containing fluorine on the first carbon atom. One compound, $CF_2ClCH_2CHFCH_2Cl$, was isolated in which the bromine atom of the original 1,1,1,4-tetrachloro-3-bromobutane was replaced by fluorine. It seems likely that a simple replacement did not occur but rather that $CF_2ClCH{=}CHCH_2Cl$ was formed and this olefin reacted with hydrogen fluoride, which is nearly always a by-product in reactions of this type. The structure of the compound was established on the basis of its failure to react with zinc under conditions where chlorine atoms on adjacent carbon atoms are known to react.

Although 1,1-difluoro-1,4-dichloro-3-bromobutane may presumably be converted to 1,1-difluorobutadiene by either of two routes

$$\begin{tikzcd}
CF_2ClCH_2CHBrCH_2Cl \arrow[r, "Zn"] \arrow[d, "KOH"] & CF_2ClCH_2CH{=}CH_2 \arrow[d, "KOH"] \\
CF_2ClCH{=}CHCH_2Cl \arrow[r] & CF_2{=}CHCH{=}CH_2
\end{tikzcd}$$

the method employed here went through the butene-1 because the product from reaction with potassium hydroxide would be low boiling, and, therefore, the chance for side reactions in this step would be minimized.

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