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Improved density gradient separation techniques using Sodium Polytungstate
and a comparison to the use of other heavy liquids

Gary L. Skipp
&
Isabelle Brownfield¹

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¹U.S. Geological Survey
MS. 916 Box 25046 DFC
Denver, Colo. 80225-0046

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INTRODUCTION

Sodium polytungstate (SPT) $3\text{Na}_2\text{WO}_4 \cdot 9\text{WO}_3 \cdot \text{H}_2\text{O}$ was introduced in 1983 as a new medium for density gradient separations (Plewinsky and Kamp, 1984). This nontoxic solid (Kazantzis, 1979) can be mixed with water to form a liquid with a fluid density that can be adjusted from pure water with a density of 1 g/cm^3 to a saturated solution with a density of 3.10 g/cm^3 . This makes it particularly useful in the density ranges for which heavy liquids such as bromoform (2.89 g/cm^3) and methylene iodine (3.10 g/cm^3) are used in the geologic laboratory. However SPT lacks the health problems associated with bromoform and methylene iodine (Riedmiller and others, 1984; Hauff and Airey, 1980; Muir, 1977).

Sodium polytungstate has other advantages. It is noncorrosive, has a pH of 6 (Gregory and Johnston, 1987), and it is stable in the pH-range of 2-14. Unlike the flammable solvents used to dilute or wash other organic heavy liquids SPT can be easily reclaimed and reused by a water wash. Because SPT is non toxic, separations may be performed without the use of a fume hood and personal protective equipment. SPT is hydrophilic improving the wettability of mineral grains thus preventing rafting, a common problem with most halogenated hydrocarbons. The solution is transparent and easily prepared.

Disadvantages with SPT include: high viscosity, rigorous sample preparation, dehydration of the SPT, longer grain settling time, and long recovery time for the SPT wash generated in a separation.

The intent of this paper is to familiarize the reader with a separation technique using SPT, compare filter paper rates, and compare heavy mineral recoveries using SPT, bromoform, and methylene iodine. Mineral reactions with SPT were also investigated. The reader is also directed to other methods and applications of separations in articles by Krukowski (1988), Savage (1988), Gregory and Johnston (1987), Callahan (1987), Torresan (1987), and Plewinsky and Kamp (1984). Experiments with SPT were conducted to determine the speed and accuracy of SPT as compared to bromoform and methylene iodine.

SAMPLE PREPARATION

Ground samples must be sieved to an appropriate size, usually dictated by the sample type or the investigator's intentions. Sample fractions less than 200 mesh (0.074mm) are separated using a centrifuge, whereas fractions greater than 200 mesh can be separated in standard separatory funnels.

Fine material (<200 mesh) must be removed by repeated water washings. Hot tap water is necessary to aid in removing soluble salts that can react with the SPT solution causing a tungsten precipitate to form in the separation. Ultra sonication of the sample for several minutes will speed cleaning but should not be used if there are fragile minerals or fossils to be preserved. The final one or two washings should be done with distilled or deionized water to remove any salts introduced by the tap water. Torresan (1987) suggested that samples be treated with dilute HCl (10%) followed by another washing with distilled water to remove calcium-rich minerals such as calcite, gypsum, aragonite, or dolomite.¹ The sample then needs to be dried, as water retained in the pore spaces is enough to significantly change the density of the sodium polytungstate solution.

SPT LIQUID PREPARATION

The solid SPT powder must be dissolved in distilled or deionized water. All labware that will come in contact with the SPT should be washed with a final distilled water rinse. Solutions can be prepared by several methods. The manufacturers provide a mass percent vs. density graph that can be read directly for the ratio of water to powdered sodium tungstate to reach the desired specific gravity (fig. 1). The density can be verified gravimetrically.

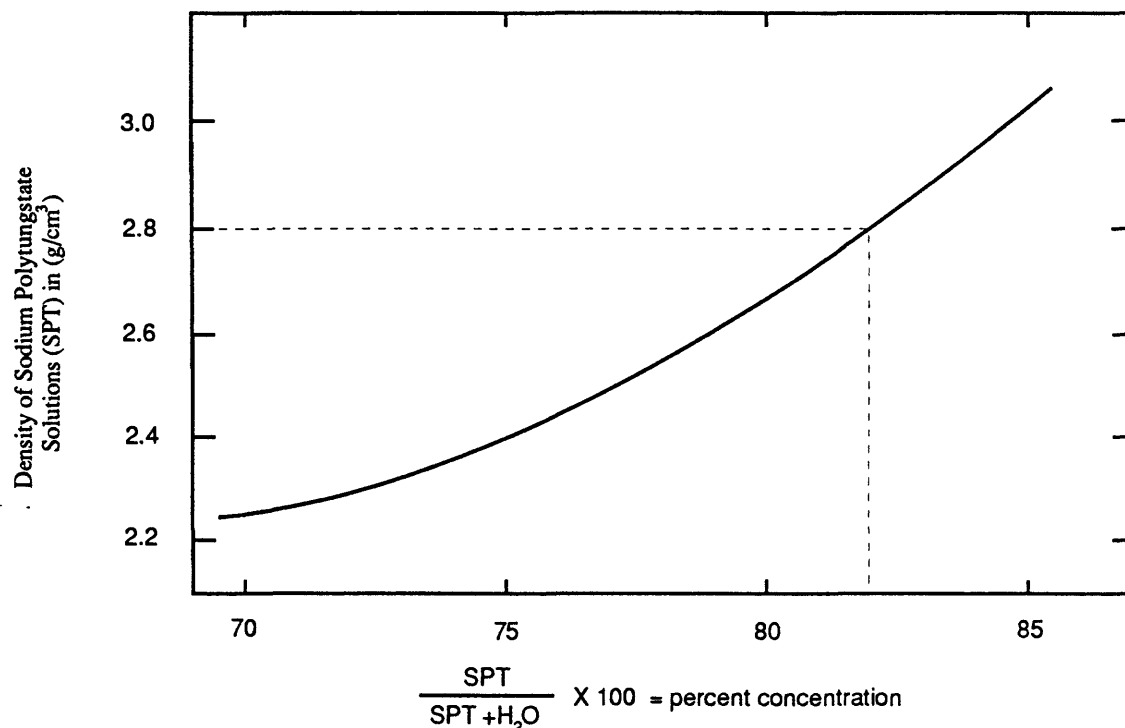


Figure 1. Density versus concentration at 20°C. Example: A SPT solution with the density of 2.80 g/cm³ at 20°C is obtained by a 82 mass percent solution (for example, 820 g solid SPT and 180 g water).

Once the appropriate proportions have been determined, mixing of the SPT solution can be done as follows: place a beaker of the water on a stirring hot plate, heat the water to approximately 60°C and add the SPT powder in small increments while stirring to dissolve most of the solid before adding more. When all the solid SPT is dissolved and has attained room temperature, the density is checked by gravimetric scale, or by sink float balls. If neither of these are available, the solution density can be checked gravimetrically by dividing the solution weight by its volume. Density can be adjusted by adding small amounts of SPT to increase the density or by adding a few drops of water to decrease the density. A larger adjustment can be made using the formula $(V_d)(\rho_m - \rho_d) = (V_l)(\rho_l - \rho_m)$ (Don Cheney, written commun., 1988) where:

- V_d = volume of dilutant
- V_l = volume of liquid at hand
- ρ_l = density of liquid at hand
- ρ_m = density of mixture
- ρ_d = density of dilutant

SEPARATION TECHNIQUES

Mineral separation methods using SPT use similar laboratory equipment as used with other heavy liquids (see appendix for equipment list). Separations can be carried out in the centrifuge or in separatory funnels. Only the separatory funnel technique will be discussed in this paper. The reader is referred to Callahan (1987), Torresan (1978), and Plewinsky and Kamp (1984) for centrifuge methods.

In the higher density ranges (2.8-3.1 g/cm³), SPT is very viscous (fig. 2). This increases grain settling time, relative to the organic heavy liquids, and the amount of stirring necessary for a separation. Higher density solutions are sensitive to evaporation of water that will cause a significant change in density and may cause the SPT to recrystallize. Therefore, one should cover all phases of the SPT separation to prevent evaporation. A hard crust may form on exposed surfaces and require redissolving. It is recommended by the manufacturer that only glass, plastic, or stainless steel be used with SPT. It was noted by Gregory and Johnston (1987) that dried SPT will adhere to glass and may cause breakage (Savage, 1988), but it will easily flake off plastic.

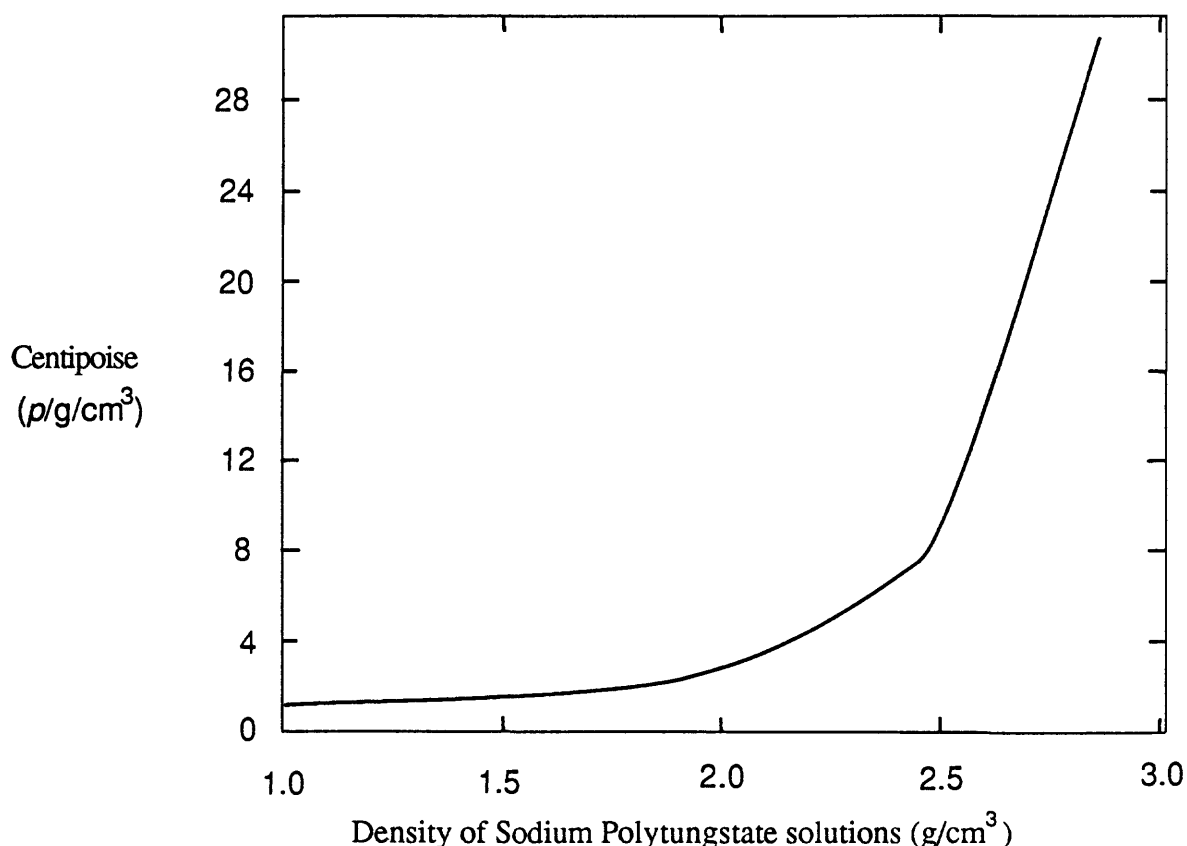


Figure 2. Viscosity of the sodium polytungstate solution visuous its density at 25° C. Modified from manufacturer's data (Sometu[®]).

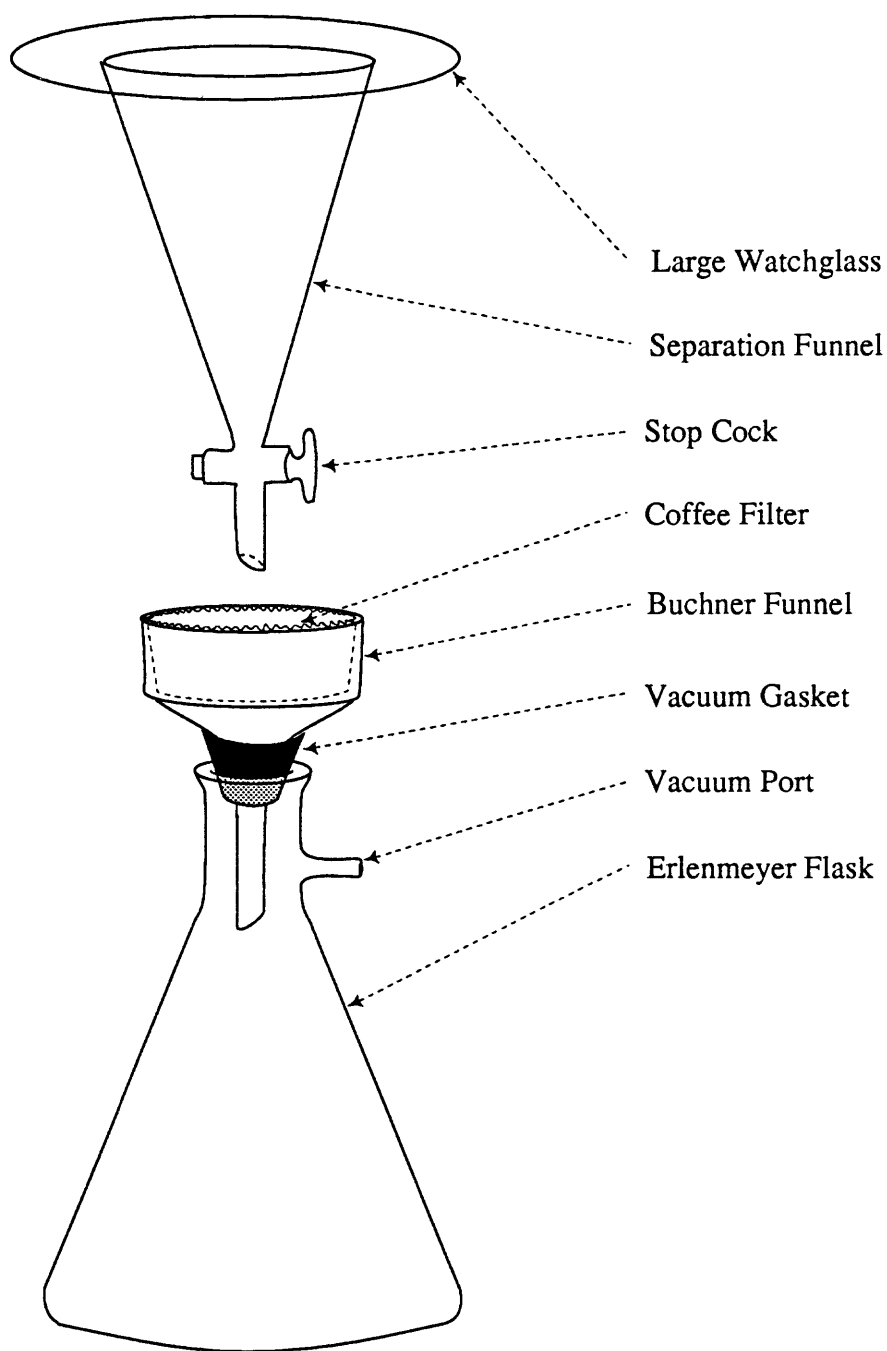


Figure 3. Separation and filtration equipment used for separation with sodium polytungstate.

In addition to the standard separation technique, the Buchner funnel is used in place of the standard conical funnel (fig. 3). This serves three purposes: 1) it increases the filtration surface area allowing a faster filtration, 2) the increase in neck size prevents crystallization and clogging, and 3) it exposes more of the sample for a thorough washing using less water.

Frequent stirring is necessary for a complete separation. Stirring intervals may range from a few minutes for the lower densities $<2.5 \text{ g/cm}^3$, to 20 minutes for the higher densities $>2.9 \text{ g/cm}^3$. Prior to draining a separate, it is helpful to slightly wet the edges of the filter paper to the Buchner funnel, because the walls of the funnel are steep in comparison to conventional funnels. This will prevent collapses of the filter paper into the filtering sample and escape of unfiltered grains. Washing the excess SPT from the sample separate with hot distilled water will decrease washing time. A vacuum pump or aspirator is recommended in all stages of filtering. This will shorten the filtration time, but the extended use of the vacuum may also cause unwanted crystallization in the funnel and filter paper.

RECLAMATION OF SODIUM POLYTUNGSTATE

The reclamation of SPT is done by evaporation of excess water until the solution is concentrated to the appropriate working density. Concentration may be done with heat, but the temperature should not exceed 60°C in order to avoid precipitation of solid sodium tungstate (Na_2WO_4) (Krukowski, 1988). Small amounts of sodium tungstate will precipitate out even at room temperature (25°C) after a few months. This precipitate is easily filtered out (see below), or the wash solution can be decanted leaving most of the precipitate behind. Evaporation can best be accomplished in large evaporation dishes or open beakers placed in a oven, hood, or on a hot plate near 60°C .

An important step in the reclamation procedure is filtering the solution before reuse. The SPT wash may contain clay-size particles and/or sodium or calcium tungstate crystals. Once the wash solution evaporates to an obvious increase in viscosity, it should be filtered. Filtering can be done through a microfilter-type filtering device. We prefer to use a plastic microfiltering device that is easily cleaned and can hold a larger volume than glass filtering devices. Krukowski (1988) and Torresan (1987) suggest using #4 Whatman qualitative filter paper and filtering as many times as necessary to remove unwanted particles; however, we found this to be insufficient to remove the fine particles. A $0.45\text{-}1.2 \mu\text{m}$ cellulose filter membrane effectively removes the fine clay-size particles. After filtration, adjust the SPT density by further evaporation, addition of solid SPT, or addition of distilled water until the solution is ready for reuse.

SPECIAL PROBLEMS

After extended use, the concentrated SPT solution must be filtered. The solution will be iridescent and cloudy. This is due to a very fine, white, calcium tungstate precipitate (CaWO_4) that forms even after a rigorous sample preparation. This is particularly true of samples containing weathered minerals or abundant clays, in which case the concentrated SPT solution may need more frequent filtering.

Calcium tungstate may contaminate the mineral separates. To remove this precipitate, wash out the soluble SPT as described above, then transfer the grains to a beaker, add water and decant before the fine precipitate settles. Repeat with several sonications. Any remaining calcium tungsten precipitate can be removed from the sample by dilute HCl or oxalic acid and should be washed with water immediately following this treatment.

If the SPT solution is brought in contact with reducing agents, the solution will turn gun-barrel blue. Elemental iron, often introduced during sample grinding, and rubber (Torresan, 1987) will cause this change in color.

Krukowski (1988) suggested that contact of SPT with iron sulfides be minimized. However, we found that pyrite, marcasite, pyrrhotite, and greigite as well as other common iron-bearing minerals (for example, magnetite, ilmenite, siderite, and hematite) did not effect the color after being in contact with the SPT solution for over 24 hours. For solutions that have changed color, let the solution stand over night in an open container or add a few drops of H_2O_2 (Krukowski, 1988) and this will clear the solution. This oxidation does not affect the density of the solution. Additionally, water-soluble dyes, inks, or markers will discolor the solution permanently (Torresan, 1987).

TECHNIQUE EVALUATION

Several experiments were performed to find the most effective filter paper for mineral separations because the higher viscosity of the SPT greatly increases filter time. Other tests were performed to verify the heavy mineral sample recovery of SPT in comparison to bromoform and methylene iodide. Mineral reactions of calcite, gypsum, and aragonite in a SPT solution were observed. These tests indicate that SPT is not a neutral solution as suggested by the manufacturer and others.

Types of filter papers

The first test measured the flow rates of various types of filter papers. Ten milliliters of the SPT solution was passed through the various filter paper types. The test was performed for each filter type with solution densities ranging from 2.8 to 3.1 g/cm^3 , the range most used in the geologic laboratory. Additional tests were performed on filter papers that were wetted (approximately 10 minutes) prior to the separation and on filter papers that were wetted and allowed to dry overnight (wet/dry). All filtration rates were determined by gravity filtration; no suction was applied.

The filter tests detected large differences between filter types and on filter pre-treatment (figs. 4, 5, and 6). The coffee filters suggested by Krukowski (1988), Callahan (1987), and Gregory and Johnston (1987) proved to be slower than expected in the higher densities ($>3.0 g/cm^3$), but faster in the lower ($<3.0 g/cm^3$) densities. The filter rates (Whatman #1, #4, and Melitta®) for the densities less than 3.0 g/cm^3 confirm the results of Gregory and Johnston (1987). The overall rates of filtration increased using the wet/dry filter papers. In general, the wetted-filter paper rates increased by an average of 23% and the wet/dry filter paper rates increased by 45%. The most consistent filter paper rate throughout the density ranges in all conditions was obtained with the Sharkskin and the VWR #54 (figs. 4, 5, and 6).

Mineral recovery

The relative amount of heavy minerals recovered using the SPT solution, bromoform, and methylene iodine was determined using Pikes Peak granite, metamorphic gneiss, and placer beach sandstone samples. The samples were sieved (60-200 mesh), washed, sonicated, and split into weights approximately 20 grams. The densities of SPT and bromoform or methylene iodine were adjusted to equivalence over the range of 2.7 to 3.1 g/cm^3 . A sample split was then added to 250 ml of each heavy liquid of a specific density and stirred until the separation was complete. The separates were washed with

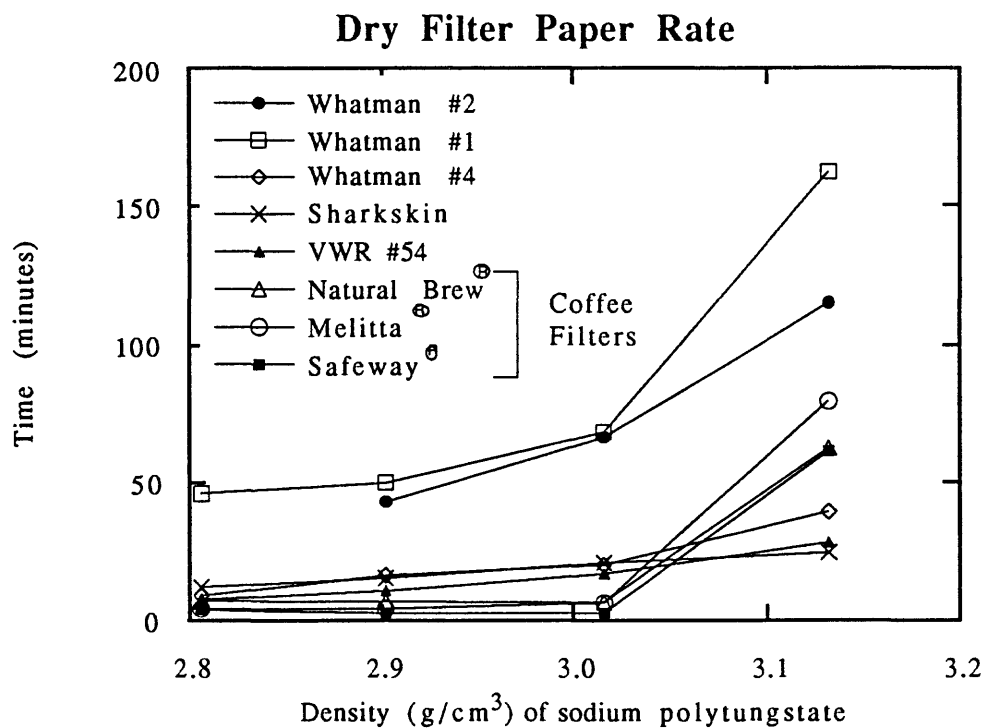


Figure 4. Graph of density versus the time required for 10 ml of sodium polytungstate to pass through dry filter paper.

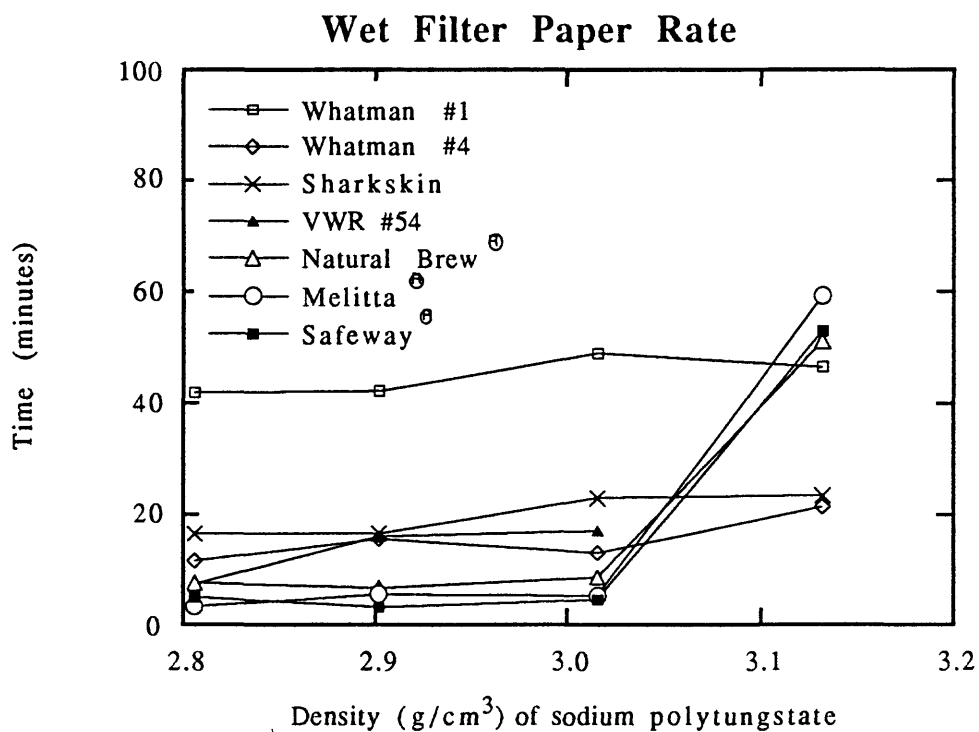


Figure 5. Graph of density versus the time required for 10 ml of sodium polytungstate to pass through wet (H_2O) filter papers.

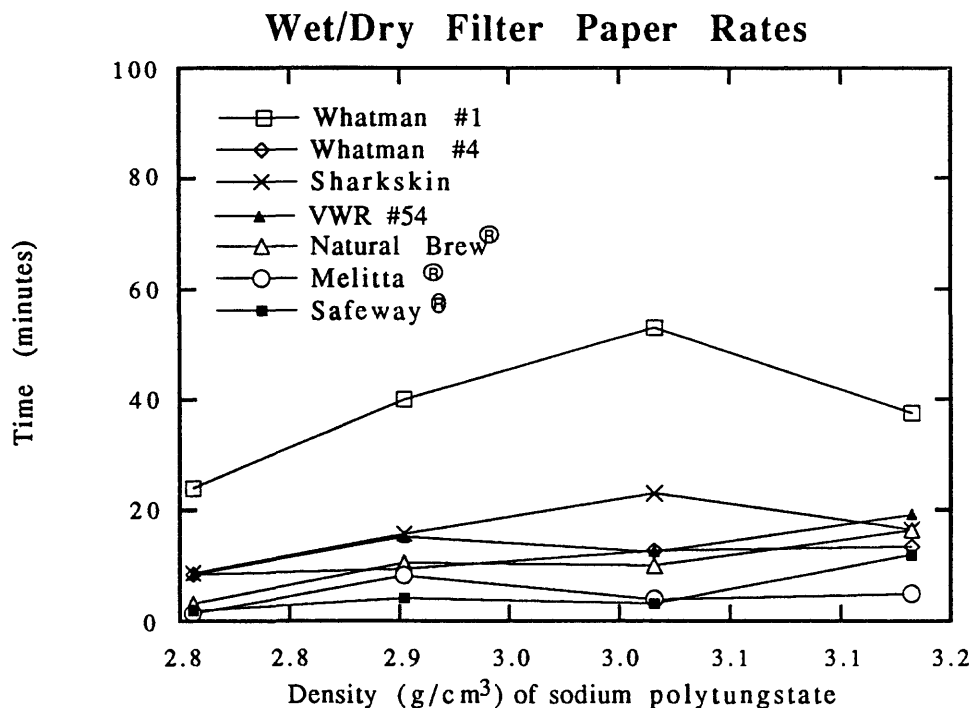


Figure 6. Graph of density versus the time required for 10 ml of sodium polytungstate to pass through a filter wetted with distilled H₂O and dried overnight.

hot distilled water (SPT separate) or acetone (bromoform or methylene iodine separate), dried, and weighed.

A comparison of heavy mineral recovery by SPT to methylene iodine and bromoform for the granite and the schist samples showed similar results (figs. 7 and 8). The percent of heavy minerals recovered from the schist samples is very similar. The granite sample, using the SPT, had a slight decrease in the percent recovery in densities $>3.0 \text{ g/cm}^3$ with a maximum difference of 1.2% at 3.1 g/cm^3 . The sandstone data were inconsistent with that of the granite and schist (figure 9 and 10). Two experiments were performed with the sandstone sample: one using a 10 gram sample and the other using a 20 gram sample. Overall, the SPT solution shows a close similarity in the recovery of heavy minerals as compared to bromoform and methylene iodide (Figs. 7, 8, and 10). A disadvantage with SPT is that densities $>3.0 \text{ g/cm}^3$ have an average separation time of 1 hour and 40 minutes as compared to 15 minutes for the methylene iodide. For densities $<3.0 \text{ g/cm}^3$, the SPT separation time decreased to an average of 30 minutes. The average separation time for the bromoform and methylene iodide at these densities remained the same (15 minutes). However, employing the wet/dry filter paper technique (as discussed previously) to the SPT separations would decrease its separation time by 10-15 minutes.

Coffee filter pore space

A concern when using the coffee filters in place of the analytical filters is the loss of grains through the larger inconsistent pore spaces. A test was designed to determine what size fraction and quantity will pass through the coffee filters. Several brands of coffee filters were used to identify any

Heavy mineral recovery from a granite

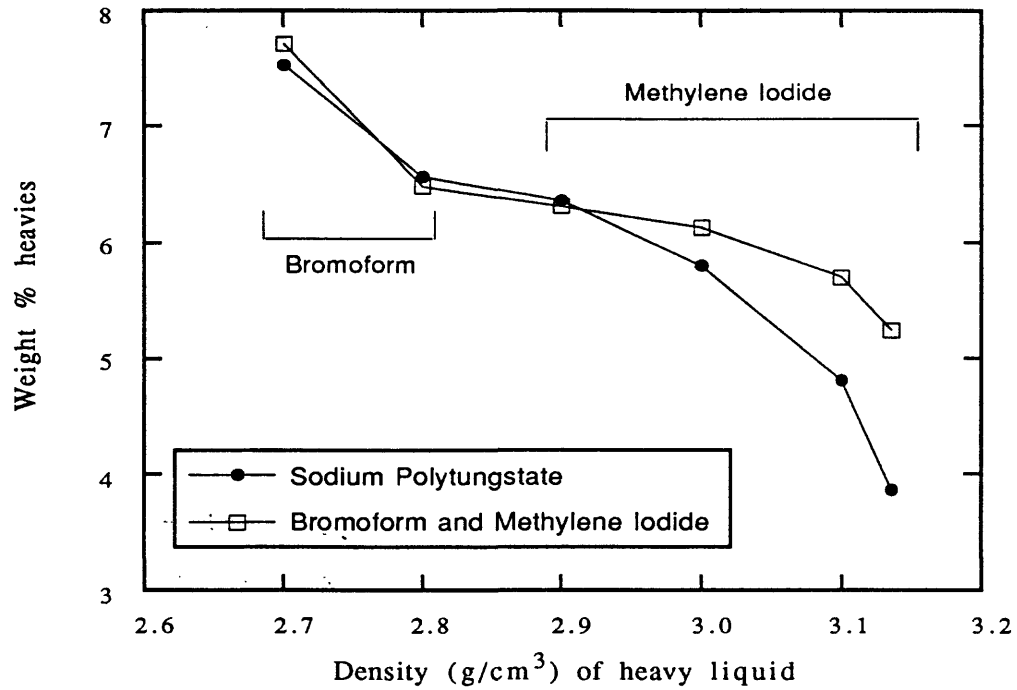


Figure 7. Graph of density versus the percent heavies recovered from a 20 gram sample using sodium polytungstate, bromoform and methylene iodide.

Heavy mineral recovery from a schist

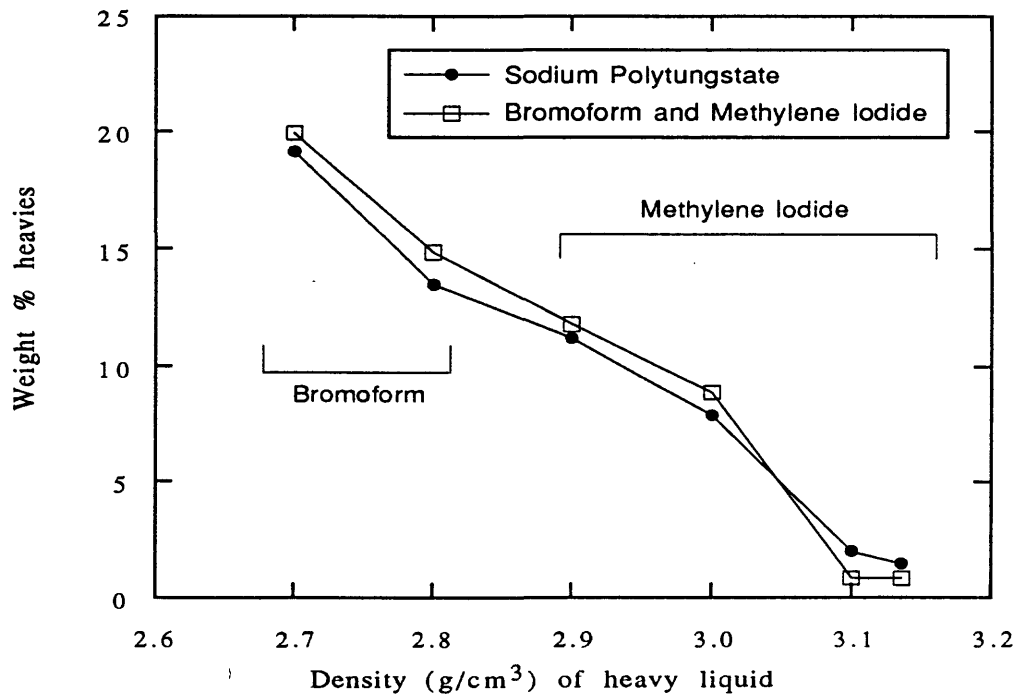


Figure 8. Graph of density versus the percent heavies recovered in a 20 gram sample using sodium polytungstate, bromoform and methylene iodide.

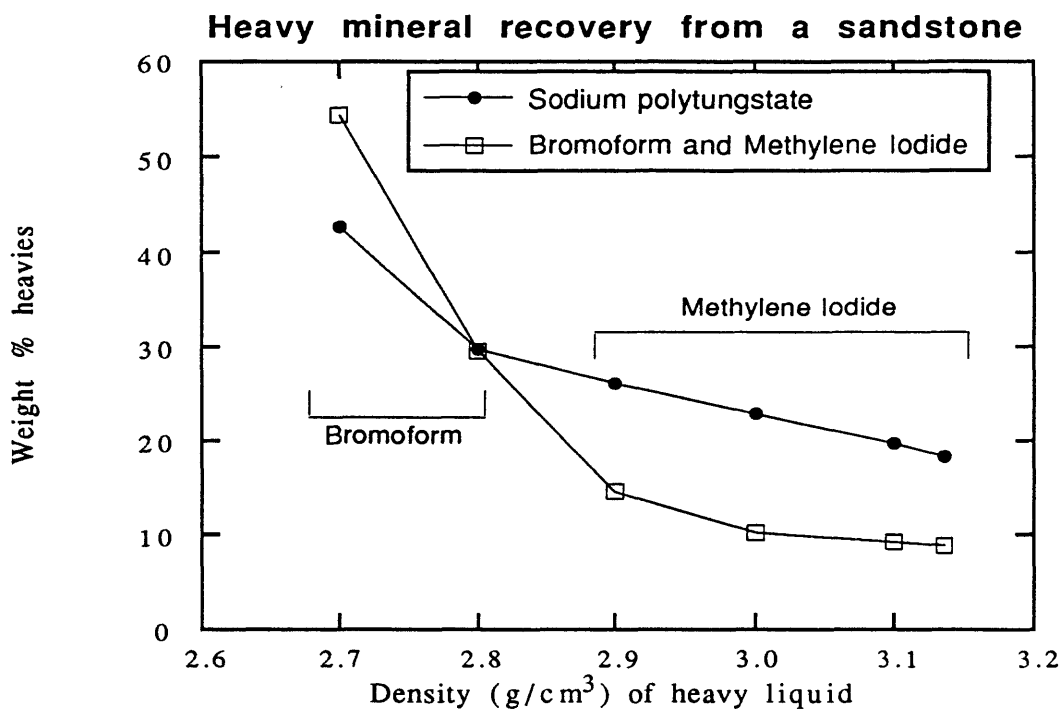


Figure 9. Graph of density versus the percent heavies recovered in a 20 gram sample using sodium polytungstate, bromoform and methylene iodide.

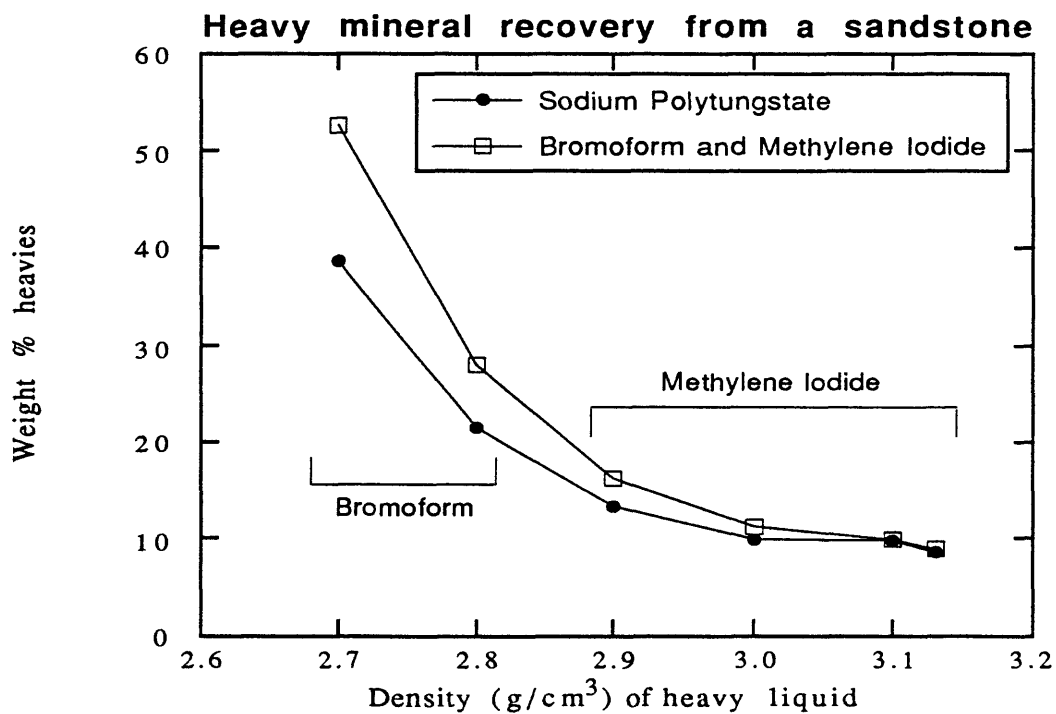


Figure 10. Graph of density versus the percent heavies recovered in a 10 gram sample using sodium polytungstate, bromoform and methylene iodide.

inconsistencies among brands. Quartz sand was ground and sieved into 7 size fractions ranging from >100 to <200 mesh. Each fraction was weighed to determine the relative abundance of each fraction. A 10 gram split was placed in a Buchner funnel with a coffee filter and set up to simulate actual sample processing. Suction was applied and a spray of distilled water applied to agitate the grains. The effluent was collected then both wet and dry sieved. All fractions were then weighed.

The <200 mesh is the only fraction that had a significant measurable amount of weight loss (table 1). The Melitta® brand lost twice as much in the <200 mesh fraction than the other two brands (table 1). Overall, the coffee filters performed well; they are stronger than most analytical grade filter papers when wet, and they fit nicely into the Buchner funnels without modification. Analytical filter papers take some finesse to fold and accommodate Buchner funnels. As shown by the filtration test rates, the coffee filters have one of the fastest separation rates especially in the <3.0 g/cm³ densities.

Partical size in millimeters	Amount lost in grams						Total beginning weight	Total ending weight
	>.15	.15-.125	.125-.105	.105-.088	.088-.074	<.074		
Type of coffee Filter								
Safeway#1	0.0002	0	0.001	0.0002	0.0003	0.1283	9.902	9.9037
Safeway#2	0.0004	0.0002	0	0.0004	0.0005	0.2095	10.015	10.0165
Natural brew#1	0	0	0	0	0	0.121	10.04	10.04
Natural brew#2	0	0	0.0001	0.0003	0.0003	0.1427	10.034	10.035
Melitta#1	0.0001	0.0003	0	0.0003	0.0002	0.5612	10.039	10.039
Melitta#2	0.0004	0.0003	0	0	0.0003	0.3249	10.049	10.0491
Percent of each fraction in sample	35.80%	2.67%	10.82%	8.24%	4.00%	39.60%		

Table 1. Weight fraction of ground quartz lost by coffee filters and the percent of that fraction in the total sample.

Mineral reactions

Reactions between SPT and calcite, gypsum, and aragonite are discussed by Bayer and Wiedemann (1989). We conducted a practical test simulating actual separation times and densities. Crystals of calcite, gypsum, and aragonite were placed in a petri dish containing SPT solution (2.9 g/cm³) and removed at intervals of 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours. Each crystal was weighed before and after and observed with the binocular microscope.

The calcite, gypsum, and aragonite crystals placed in the SPT solution showed etching on crystals after 1 hour or longer. Crystal overgrowth was also observed on the crystals after longer duration's. Crystals in longer than 1 hour showed measurable loss in weight (see table 2). Additional experiments were performed allowing grains to remain in a SPT solution of 2.2 g/cm³ and

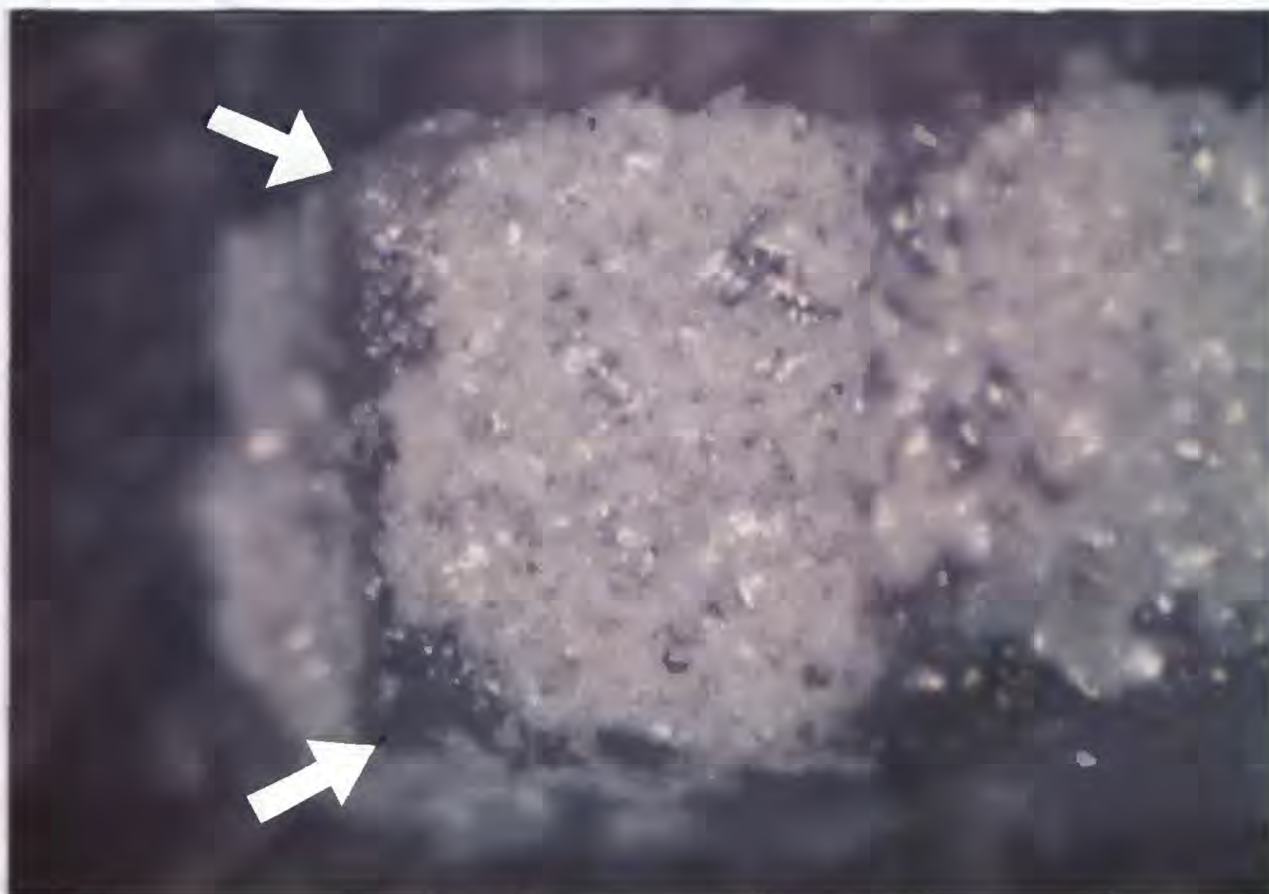
2.9 g/cm³ for several days. Crystal etching and simultaneous crystal growth were pronounced (fig. 11a). The most interesting result was that gypsum showed signs of dissolution within one hour, and in several days (fig. 11b) the gypsum crystals had totally dissolved in the 2.2 g/cm³ solution. No reaction was noted with noncarbonate minerals. A fresh solution of SPT was prepared from the manufacturer's container and distilled water (pH 5.5). The density was gradually increased from 2.29 g/cm³ to 3.14 g/cm³ by adding more solid SPT and monitored with a pH electrode (fig. 12). It was surprising to observe an average pH of 4.4 considering that the manufacturer suggested a pH of 6. This pH is undesirable in the most typical separations and will need adjustment before use.

Crystal type and time (in hours)	Initial sample weight (in grams)	Final sample weight (in grams)
Calcite:		
0.5	0.1375	0.1378
1	0.0744	0.0746
3	0.1482	0.1482
6	0.3739	0.374
24	0.2719	0.2712
Gypsum:		
0.5	0.0466	0.0354
1	-	-
3	0.103	0.102
6	0.162	0.1605
24	0.0658	0.063
Aragonite:		
0.5	0.0355	0.0354
1	0.1583	0.1586
3	0.0248	0.0245
6	0.0709	0.0706
24	0.0852	0.085

Table 2. Weights of crystals before and after exposure to a SPT solution having a density of 2.99g/cc. (Dash, no data)



A



B

Figure 11. Photomicrographs of calcite (a) and gypsum (b) crystals that were submerged in a 2.22 g/cm^3 sodium polytungstate aqueous solution for six days (calcite) and one hour (gypsum). Note the dissolved crystal edges (arrows) on calcite and a fine coating of calcium tungstate crystals coating the rest of the crystal. The gypsum crystal clearly shows etching (arrow) along crystal lattice planes after only one hour.

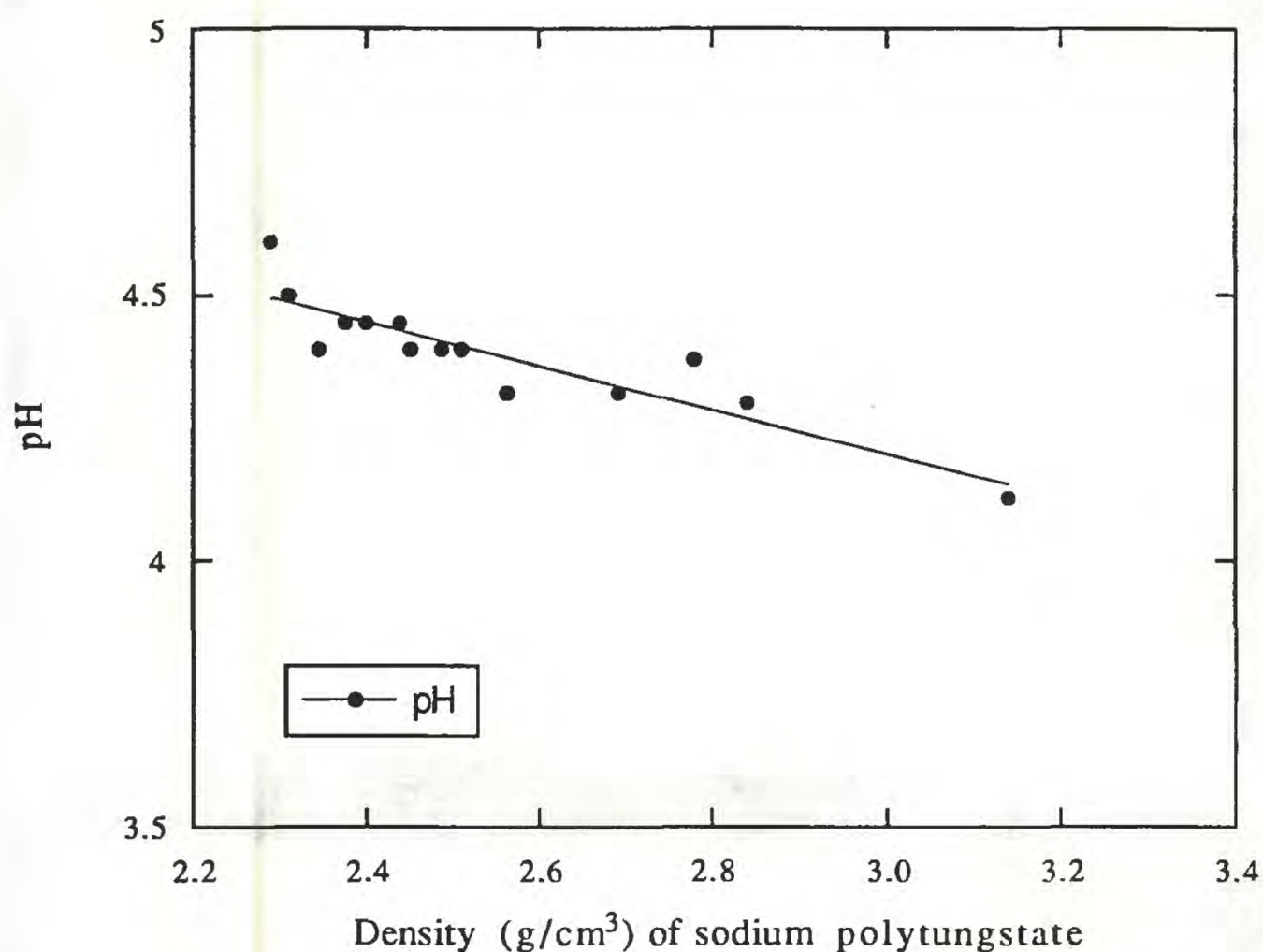


Figure 12. Density versus the pH of sodium polytungstate.

SUMMARY

Sodium polytungstate is a useful and practical medium for density gradient mineral separations. The nontoxic nature of SPT outweighs additional time required for separations. The filter paper rate experiment showed coffee filters are best in the $<3.0 \text{ g/cm}^3$ densities and the analytical filters (Sharkskin and VWR #54) are best for densities $>3.0 \text{ g/cm}^3$. The comparison of heavy minerals recovered from SPT, bromoform, and methylene iodine were close enough that SPT should be adopted for most mineral separates in the geologic laboratory. An exception is samples containing calcite, aragonite, and gypsum if these minerals are of importance. Further studies are needed to identify additional minerals that may be soluble or react in the SPT solution. The test results presented will help technicians identify the limitations, special problems, and streamline the mineral separation process.

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APPENDIX

Equipment list:

- Separatory funnel
- Buchner funnel
- Erlenmeyer flask with suction port
- Vacuum pump or aspirator (make sure aspirator has directional valve as not to back up and contaminate SPT)
- Standard conical funnel
- Stirring rod or spatula
- Watch glass, parafilm, plastic wrap, or anything adequate to cover SPT concentrate
- Small beaker (for holding stirring rods and catching excess SPT)
- Vacuum gaskets
- Wash bottles
- Drying equipment (not necessary but helpful)

See Figure 3 for separation equipment set up.