UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

The use of sodium polytungstate in heavy mineral separations

by
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INTRODUCTION

Sodium polytungstate is a water-miscible, nontoxic, high-density compound (up to 3.1 g/cm^3) that has successfully been used as a substitute for the toxic compounds bromoform and tetrabromoethane for both mineral and conodont separations (Callahan, 1987; Krukowski, 1987a and b; Kazantzis, 1979; Sax and Lewis, 1986). Krukowski (1987a) also cites the use of sodium polytungstate by the New Mexico Bureau of mines as a medium to separate various feldspar species from one another, and to segregate inorganic mineral fractions (ash) from coal.

Bromoform and tetrabromoethane, the most widely used heavy liquids, are toxic, halogenated hydrocarbons. Exposure to these compounds can cause unconsciousness, respiratory failure, irreversible damage to the liver, kidneys and lungs, and even result in death (Cahallan, 1987; Carver, 1971; Hauff and Airey, 1980; Krukowski, 1987a; and Sax and Lewis, 1986). Sodium polytungstate is a substance that can replace these two toxic compounds for most separations.

Sodium polytungstate is available in either liquid or powdered form from:

SOMETU
Falkenreid 4
D-1000 Berlin 33
West Germany

Cost is about DM 150 ($70 U.S.) per kilogram. According to data provided by the manufacturer (appendix 1) and Callahan (1987), a 1250 g solution with a density of 2.90 g/cm^3 can be made by adding 250 g of distilled water to 1000 g of powdered sodium polytungstate.

USGS tests with sodium polytungstate and the experiences noted by other users shows that sodium polytungstate is easily miscible to densities up to 2.7 g/cm^3, but above this it becomes difficult to work with owing to increased viscosity. Also, sodium polytungstate has certain characteristics that may make it not be directly substitutable for the more typically used heavy liquids (Krukowski, 1987a). These problems include its viscosity at densities above 2.7 g/cm^3, and its interaction with free Ca^{++} to form calcium polytungstate, that can interfere with chemical analyses.

METHODOLOGY

A variety of separation and recovery techniques has been described by Callahan (1987) and Krukowski (1987a). Persons already familiar with heavy-liquid separation techniques should have no difficulties converting to sodium polytungstate once they have familiarized themselves with its characteristics. Laboratories set up for heavy-liquid separations can use the same general techniques and apparatus when using sodium polytungstate. A list of do's and dont's and a description of separation and recovery techniques are detailed in this report. It is suggested that new users read Carver (1971, p. 427-452), Callahan (1987), Krukowski (1987a) and references cited therein, to familiarize themselves with the use of heavy liquids for separations.

Do's and Don'ts

1. Use only distilled water for mixing the polytungstate solution and rinsing samples and lab ware.

2. Wet-sieve your samples well to remove the grain sizes not needed for your analysis. Use as coarse and narrow a range of particle size as possible.

3. Use only cleaned and rinsed (with distilled water) plastic, glass or stainless steel lab ware (plastic works the best).

4. Use only steep-sided, sealable separatory funnels or centrifuge tubes to prevent grains from sticking to the walls. If using a separatory or regular funnel use one with as wide an exit diameter as possible to prevent clogging of the funnel pore.

5. Keep the sodium polytungstate density as low as possible to prevent viscosity problems.

6. Adjust the specific gravity by bringing it down from a higher specific gravity to a lower one by the addition of distilled water.

7. Keep the sodium polytungstate sealed and keep the exposure time to air to a minimum as it will prevent evaporation. This will keep the sodium polytungstate from precipitating out of solution and interfering with the separation.

8. Avoid exposing the sodium polytungstate solution to free calcium. Exposure will form the insoluble precipitate calcium polytungstate and can clog pores in the filter paper and contaminate samples used in chemical analyses. The sample material to be separated should be free of all soluble components including Ca^{++}. Users and the manufacturer suggest cleaning samples with HCl and then rinsing with hot distilled water.

9. Be careful of water-soluble dyes or cements on labels and tape as they permanently discolor the

sodium polytungstate solution.

10. Do not allow the sodium polytungstate solution to come in contact with any reducing agents (i.e. black rubber stopper particles) as a blue color will result. The color, however, does not influence the density of the solution.

11. Use vacuum aided filtration if possible during recovery of the sodium polytungstate solution following separation, as the small filter and funnel pores may clog with sodium polytungstate precipitating out of solution. If vacuum-aided filtration is not available then dilution of the sodium polytungstate solution with distilled water will prevent the clogging of filter and funnel pores and decrease filtration time.

12. If vacuum-aided filtration is employed be careful to monitor the amount of vacuum that is placed on the filtration apparatus, as the filter paper may tear during the process.

Sample Separation Procedure

The use of sodium polytungstate for mineral separations should pose no problems for users that have prior experience with heavy liquids and mineral separations. Users unfamiliar with the use of heavy liquids for mineral separations are referred to Allman and Lawrence (1972; p. 191-224) and Carver (1971; p. 427-452).

Pretreatment of Samples

Samples should be disaggregated before sieving. Methods for sample disaggregation can be found in Carver (1971). Following disaggregation, the samples should be size segregated to as coarse a size fraction as possible. According to Carver (1971), it is desirable to restrict heavy mineral studies to a single size class narrow enough to produce uniform optical effects and to reduce or eliminate variations in heavy mineral proportions caused by differences in grain size. It is also desirable to use as coarse and narrow a size as possible because finer grained samples tend to have more free Ca^{++}, and may contaminate the sodium polytungstate solution.

Following segregatation all free Ca^{++} should be removed by washing in dilute HCl (10%), followed by rinsing with distilled water. Distilled water should always be used because free Ca^{++} will combine with the sodium polytungstate to form the insoluble residue calcium polytungstate. Calcium

polytungstate interferes with mineralogical and chemical analyses, and may clog the filter paper used for reclaiming the sodium polytungstate following a separation.

Preparation of the Sodium Polytungstate Solution

If powdered sodium polytungstate is used, it should be mixed into solution using distilled only water. To obtain the proper density the user can follow a chart and formula provided by the manufacturer (fig 1 or appendix 1). According to figure 1, a 2.5 g/cm^3 corresponds to a 70% mass solution, or 70 g of powdered sodium polytungstate diluted in 30 g water. Based on my personal experiences and that of other users, it is easy to make solutions with densities up to 2.7 g/cm^3, and substantially more difficult to mix above this. Mixing higher densities is facilitated with the use of a magnetic stirrer/hot plate combination. Temperature setting should be low and sodium polytungstate should be added in small amounts until all is dissolved.

Solution density can be checked with a specific gravity balance or a calibrated sink/float standard. Fine tunning the solution is then accomplished by the addition of either distilled water a few drops at a time to lower the solution density, or by placing the solution into a large, open beaker and then placing it into an oven at low temperatures (60-70°C), to evaporate off the excess water thereby raising the density. It is important that the density of the solution be adjusted only when at ambient temperature, as temperature will affect the solutions density (Krukowski, 1987a). Based on my experience and that of Krukowski (1987a), it is best to start with densities exceeding 2.8 g/cm^3 and work down to the required density by adding the distilled water a few drops at a time.

Gravity Separation

Krukowski (1987a) describes in detail the gravity separation method for sodium polytungstate. Examples of typical gravity separation apparatus are displayed in figure 2. Figures 3 and 4 depict apparatus used by John Callahan of Appalachian State University and Norman Savage of the University of Oregon (personal communication). Krukowski (1987a) uses steep-sided, sealable funnels (fig. 2),

whereas Callahan uses the system diagramed in figure 3. Callahan (personal connunication) prefers a funnel with a large exit pore to speed up the separation and prevent the clogging that some of the smaller diameter funnels are susceptible to. Figure 4 illustrates the method employed by Norman Savage (personal communication) for the complete process both separation and recovery.

Steep-sided separatory funnels are recommended as they prevent mineral grains for sticking to their walls. They should be sealable with either screw-top lids, parafilm M laboratory tape, or other wrap or cover. This seal will prevent the sodium polytungstate from crystallizing out of solution owing to evaporation, thereby interfering with the separation. Fill the separatory funnel with 150-300 ml of the sodium polytungstate liquid, or enough to provide a column of fluid that is easy to work with, generally between 5 and 15 cm high (Krukowski, 1987a). Familiarity will help determine the amount one starts with. Funnels without ribs or flutes are desirable for this process because they tend to interfere with the stirring that is required for a complete separation (Krukowski, 1987a).

Add a preweighed sample into the sodium polytungstate. Gently stir the sample with a stirring rod to suspend and distribute the sample throughout the fluid so that all grains are properly wetted. Seal the funnel and wait about 3 hours for the heavy mineral grains to begin sinking to the bottom. Continue stirring the suspension once every three hours, using a squirt bottle filled with polytungstate solution to rinse away any grains that remain stuck to the stirring rod or sides of the separatory funnel. Remember to keep the separatory funnel sealed to prevent evaporation of water thereby causing the sodium polytungstate to crystallize out of solution and sink, dragging down the lights into the heavies below. The separation should be complete in about 9 hours.

Unstop the funnel and drain the heavy mineral concentrate and sodium polytungstate solution into a funnel fitted with filter paper, and suspended over or attached to a flask to capture the undiluted sodium polytungstate filtrate. Filtration can be aided with an aspirator or vacuum pump. In USGS tests a vacuum with Whatman #4, 24 cm filter paper has been used successfully for filtration. Callahan (1987) and Krukowski (1987a) prefer basket type coffee filters that allow higher flow rates, thus speeding up recovery time. USGS tests confirm their results.

Use a separate flask to capture diluted solution and washings. Following the capture of the heavy mineral filtrate, remove the flask used to recover the undiluted solution and replace it with a flask for diluted sodium polytungstate. Rinse the heavy mineral concentrate with distilled water to recover any sodium polytungstate that may be retained in the concentrate or the filter paper.

Gravity filtration is also facilitated by diluting the filtrate with distilled water. This decreases viscosity and increases flow rate, but also results in a larger volume of diluted sodium polytungstate requiring evaporation. Slow, undiluted, and unaided gravity-filtration can cause the filter paper and funnel pores to become clogged with sodium polytungstate owing to the low flow rates and consequential evaporation of water. The user must use judgement about when and how much water to add. Do not use so little water that the funnel and filter pores clog, nor so much as to end up with a large volume of diluted solution.

Using the squirt bottle rinse the sides of the separatory funnel with pure sodium polytungstate solution and let the remaining heavies that are stuck to the sides of the funnel separate out. Filter and rinse as described above. After the un- or slightly-diluted sodium polytungstate has filtered through the filter paper, remove the flask containing the undiluted solution and replace it with a flask for diluted sodium polytungstate and washings. Wash and rinse the filtered concentrate and filter paper thoroughly with distilled water to remove and recapture all the remaining sodium polytungstate. When completely rinsed, dry and weigh the heavy mineral concentrate.

To keep the sodium polytungstate solution close to the required density, keep the slightly diluted or undiluted sodium polytungstate separate from the diluted solution and washings. This will decrease the recovery time spent in the recovery oven. Pour off and save the undiluted and diluted filtrate in separate, large and open beakers for recycling.

The filtering procedure is repeated for the light fraction. Remember to rinse the walls of the separatory funnel to remove all material adhering to the walls, and to keep the slightly diluted solution separate from the washings. Also, if many samples are to be processed then it is desirable to set up a multiple funnel rack that permits several samples to be handled simultaneously.

Krukowski (1987a) suggests the use of plastic (either polyethylene or polypropylene) lab ware over glass or stainless steel. Apparently the sodium polytungstate salt adheres much less tenaciously to the plastic, and is more readily cleaned.

Recycling Procedure

The recycling procedure employed by most users is schematically diagramed in figure 4. To recycle and reclaim the sodium polytungstate, the slightly diluted filtrate and washings are placed in open beakers and set in an oven to evaporate the excess water. Krukowski (1987a), Norman Savage (Univ. of Oregon; personal communication) and USGS tests shows that the oven should be set at a low temperature (60-70°C). Krukowski (1987a) states that if a hot plate is used it should be set at its lowest temperature setting. Krukowski (1987a) also has had excellent results in driving off water when placing the solution in a high airflow fume hood. The most important part to this procedure is to keep the temperature low so as not to saturate the solution to the point of efflorescence. This will cause the dehydration of the sodium polytungstate and result in its precipitation from solution.

USGS tests and that of Krukowski (1987a) show that after repeated use, the user will notice a white specular precipipate forming in the solution. Krukowski (1987a) attributes this to several causes. First, after processing between 175 and 200 samples, Krukowski found that the sodium polytungstate would dehydrate, effloresing into Na_2WO_4. This can be avoided by keeping the density as low as possible and by using low temperature heat sources when recycling. The second major cause of a precipitate is the formation of calcium polytungstate when free Ca^{++} cations are introduced into the solution either from the use of tap water or improperly prepared and washed samples. Thus, it is important to rinse all samples and lab ware only with distilled water to circumvent this problem.

Krukowski (1987a) also found that clay-size particles from muddy residues may pass through certain filters. Because of this, the sodium polytungstate should be filtered periodically with qualitative filter paper. Several filtrations should clear the solution. An alternate method would be to dilute the solution sufficiently to allow all the particles to settle responding to the lowered density. Then the uncontaminated liquid can simply be decanted off (Krukowski, 1987a). USGS tests show that a

combination of dilution and filtration through a qualitative filter paper followed by decanting works best.

Separation by Centrifugation

Users unfamiliar with the centrifugation technique are referred to Carver (1971). Callahan (1987), Stephen Forman (Univ. of Colorado; personal communication) and Edward Rhodes (Oxford Univ.; personal communication) perform certain separations under centrifugation. Callahan (1987) prefers centrifugation with fine-grained samples < 40 mesh (< 425μ). Rhodes, whose samples are in the 90-125μ size class also prefers centrifugation followed by quick-freezing of the lower few centimeters of the centrifuge tube. This allows the light fraction to be poured off easily.

The centrifuge method of heavy mineral separation is typically used for samples finer than 63μ (Carver, 1971). This method is probably superior to the gravity settling method in the use of sodium polytungstate, owing to its speed and ability to overcome the viscosity at densities above 2.5 g/cm^3. Centrifugation is not only faster than the gravity method, but it also allows more flexibility in that the centrifuge tubes can be sealed and set aside for several hours or days without any problems.

For centrifugation, strait-walled 50 ml capacity or larger, sealable centrifuge tubes with conical bottoms are recommended. Start with two or more tubes, or the number required to fill the centrifuge head. Clean and rinse each tube with distilled water, then properly label each tube. In the method of Rhodes (personal communication), sample splits between 10 and 20 grams are added to the tubes. The tubes are then filled with the sodium polytungstate fluid to the same level. Place each tube into an ultrasonic bath for several minutes to insure the proper wetting of all the grains. Next, weigh each tube to within 0.1 g of some common weight by adding the appropriate amount of polytungstate solution. This step insures a balanced centrifuge head. Remember, if using tapered or conical-bottom tubes, use the rubber cushions designed to received them. Centrifuge between 500 and 1000 rpm for several minutes. A rule of thumb is that the finer the grain size, the longer the time and the higher the speed required. Experience will dictate the time and speed, but be careful not to exceed the breaking strength of the tubes you use.

Several procedures can be used in separating the light fraction from the heavy fraction following centrifugation. Carver (1971) cites the removal of the heavy fraction with the aid of a hypodermic needle fitted with a short piece of clear tubbing on its end, but this method is tedious.

Partial freezing is another method used for recovering both the light and heavy mineral concentrates. A detailed description of this method can be found in Fessenden (1959), Scull (1960) and Carver (1971). Rhodes (personal communication) successfully employs liquid nitrogen in partial freezing. Following several minutes of centrifugation, the lower ends of the tubes are submerged in either liquid nitrogen, dry-ice or a cold-finger in an acetone or alcohol bath, such that the lower few centimeters of the solution freezes. Freezing is allowed to progress 2 to 4 cm above the heavy concentrate. USGS tests show that freezing with a cold-finger takes between 5 and 10 minutes. Following freezing, the light-mineral concentrate is simply poured off. Any lights that may adhere to the sides of the tube are easily rinsed out by flushing out the tube with a jet of sodium polytungstate solution (preferably cold) from a squeeze bottle. After the sodium polytungstate solution has filtered through a funnel fitted with filter paper the light mineral fraction can be washed, dried and weighed.

The centrifuge tube containing the frozen heavy mineral concentrate is either left to defrost and poured off into a funnel fitted with filter paper, or it can be simply diluted with water until light enough to be poured off leaving the grains behind. As in the gravity method, repeat the rinsing with distilled water to remove all the remaining polytungstate. Filter, recover and recycle the polytungstate solution as previously described.

In summary, the more one familiarizes themselves with the characteristics of sodium polytungstate, the easier it becomes to use. Users already familiar with heavy liquid separations should have no great difficulty in converting over to this method. Its non-toxicity, water miscibility and ease of use especially with centrifugation are the primary reasons for this compound's importance.

REFERENCES

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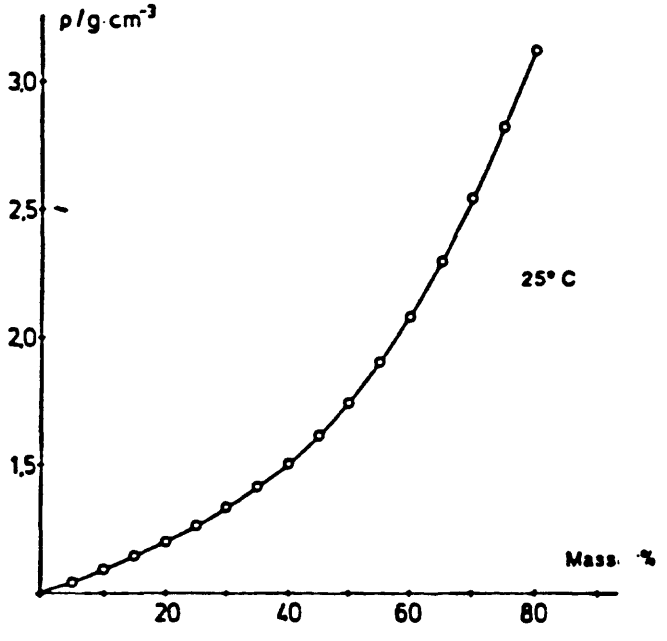
Sax, N.I., and Lewis, R.J., 1986, Rapid guide to hazardous chemicals in the workplace: New York, Van Nostrand Reinhold Co., 236 p.

Scull, B.J., 1960, Removal of heavy liquid separates from glass centrifuge tubes- alternate method: Journal of Sedimentary Petrology, v. 30, p. 626.

FIGURES



$$\text{mass\%} = \frac{\text{gram (substance)}}{\text{gram (substance + water)}} \cdot 100.$$

Example: Formation of a polytungstate solution with a density of 2.5 g/cm³

According to the diagram this corresponds to a 70 mass% solution, i.e. 70 g polytungstate + 30 g water.

Figure 1. Chart and formula used to determine solution density.

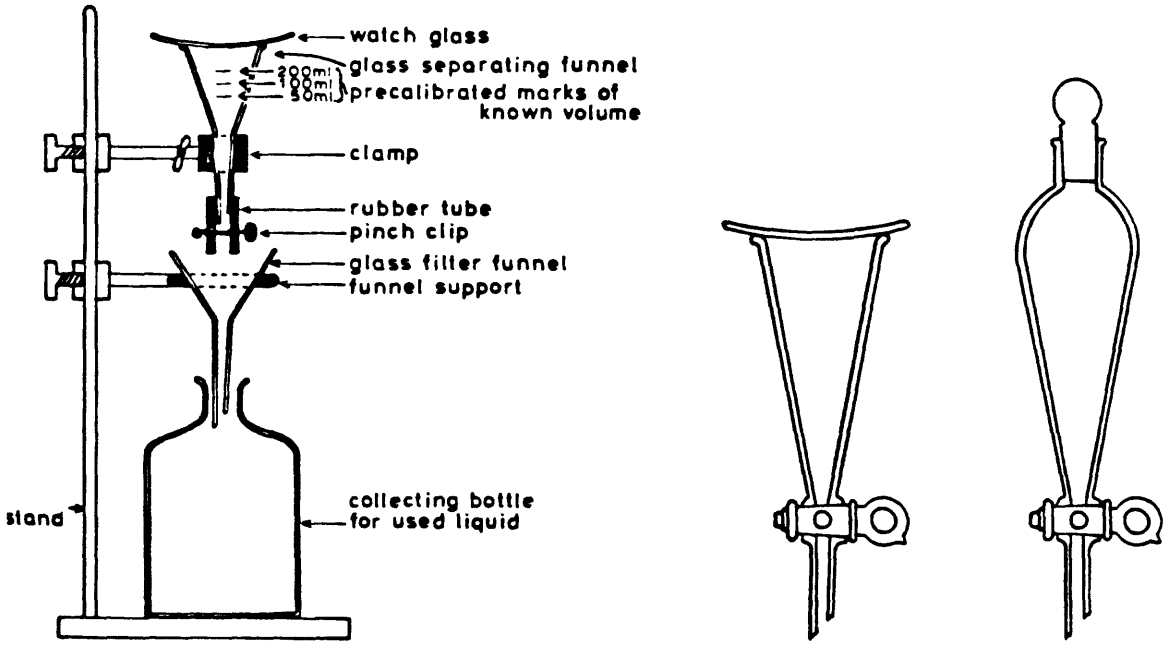


Figure 2. Typical heavy liquid separation apparatus (from Allman and Lawrence 1972).

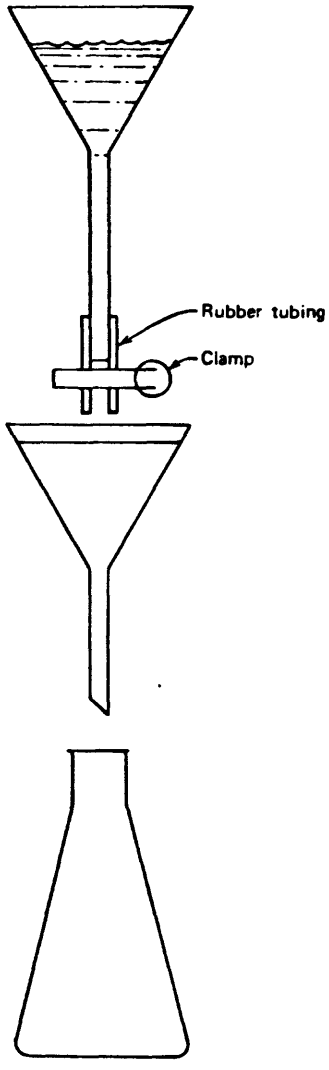


Figure 3. Separation apparatus employed by J. Callahan (personal communication).

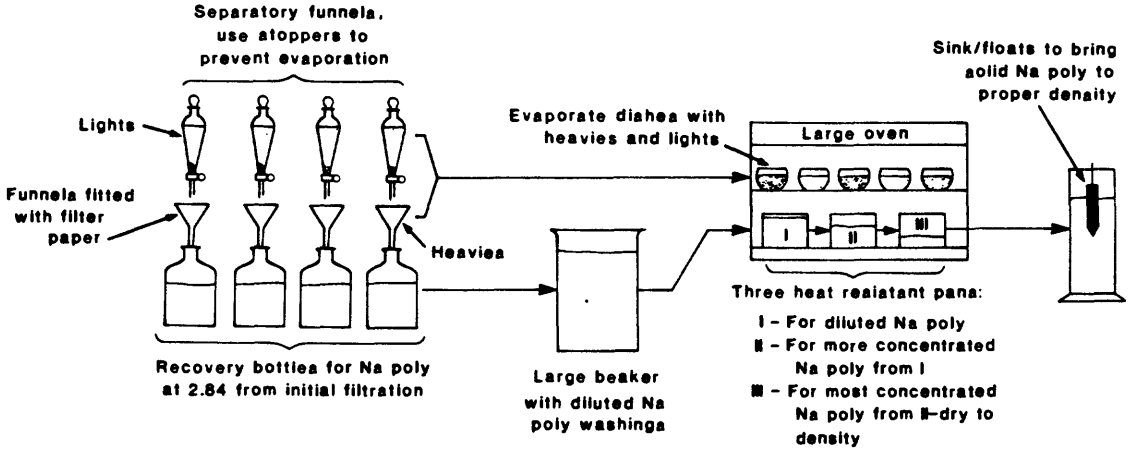


Figure 4. Schematic diagram of the complete gravity separation and recovery procedure (from N. Savage, personal communication).

APPENDIX 1

SOMETU
Falkenried 4
D-1000 Berlin 33
Telex: 0 185 443
SMT West Germany

Patented

$3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$
sodium polytungstate

do not incorporate

Advantages:

a) aqueous, neutral (pH 6) solution of the inorganic salt $3\ Na_2WO_4 \cdot 9WO_3 \cdot H_2O$.

b) Stable in the pH-range of 2-14.

c) Density adjustable from 1 to 3.1 g/cm^3.

d) Relatively low viscosity (at a density of 1.96 g/cm^3 a $ZnCl_2$ solution has a viscosity of 30.6 mm^2/sec. and a polytungstate solution of only 1.98 mm^2/sec.

e) Laboratory centrifuges can be used.

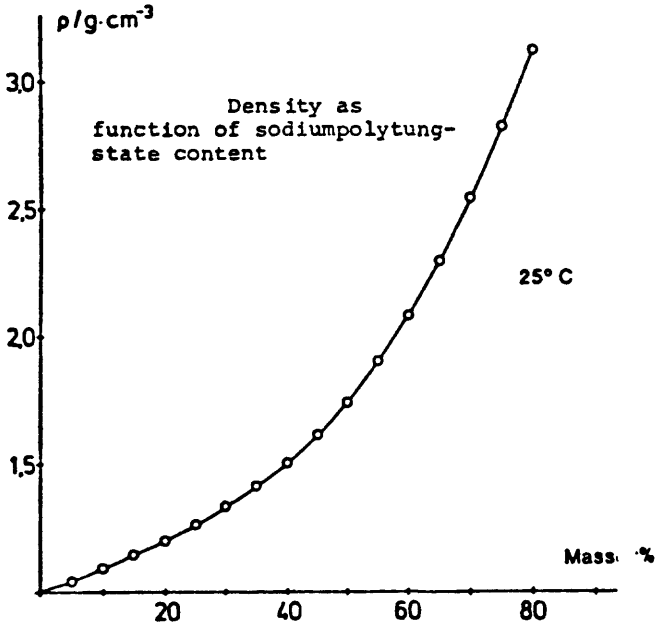
f) Reuseable

g) No obnoxious smell

h) Simple handling. Can also be discarded easily. (in small concentrations tungsten compounds improve plant growth).

i) Can be used for the isopycnic density gradient centrifugation of minerals etc. This is a totally new technology. See separat sheet.

j) According to the 1982 edition of the comprehensive Handbook on the Toxicology of Metals tungsten compoiunds are considered non-toxic, whereas the halogenated lower alkanes, in particular tetrabromoethane, are known to be cancerogenous. See separate sheet. If polytungstate is accidentally ingested all is excreted within twenty four hours.



$$\text{mass\%} = \frac{\text{gram (substance)}}{\text{gram (substance + water)}} \cdot 100.$$

Example: Formation of a polytungstate solution with a density of 2.5 g/cm^3

According to the diagram this corresponds to a 70 mass% solution, i.e. 70 g polytungstate + 30 g water.

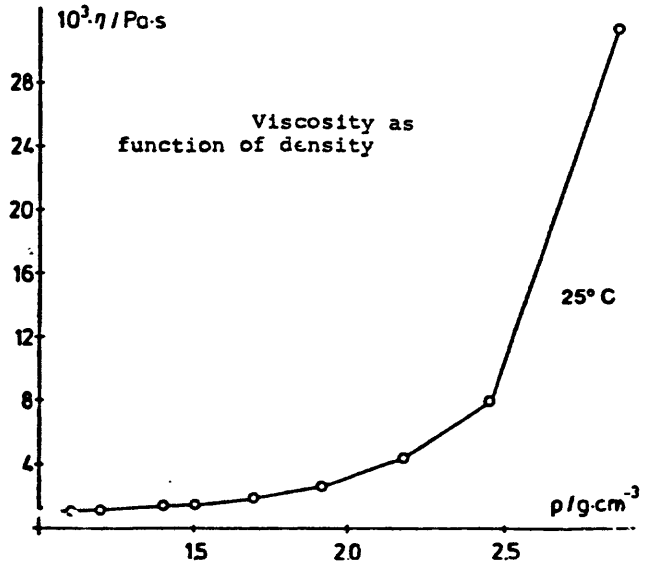
Please note the following:

a) Use only distilled or demineralized water.

b) Use only glass, plastics or stainless steel containers.

c) If possible, do not contact with reducing agents. A therefrom resulting blue color has, however, no influence on the density chosen.

d) The polytungstate solution can be recovered by washing respective particles with distilled or demineralized water and then evaporating to the desired density respectively solid polytungstate is added.



As can be derived from figure 2, the viscosity increases only insignificantly up to a density of about 2.5 g/cm^3. Accordingly also separations in the fine grain range are possible within shorter periods.

IMPORTANT: The sample material to be separated should be free of soluble components, in particular calcium ions. Otherwise insoluble calcium polytungstate is formed. A respective example are clay type minerals. If in doubt apply a thorough hot water washing.

PROPERTIES OF SODIUM POLYTUNGSTATE SOLUTIONS

Density (g/ml)	Index of Refraction	Osmolarity (mOsm)
1.08	1.3437	140
1.165	1.3540	265
1.333	1.3744	480
1.495	1.3945	710
1.661	1.4152	
2.900	1.5800	

CONDUCTIVITIES

Sodiumpolytungstate solution % (w/v)	µS	KCl % (w/v)	µS
10	4000	0.0075	40
20	6800	0.075	370
40	11500	0.75	3300
53	13800	7.5	28252
80	18500		

The solid polytungstate has the following analytical data:

	WO_3	=	86.66%
	Na	=	4.5 %
	H_2O	=	8.84%
Trace Elements:	As	<	5 ppm
	Bi	<	2 ppm
	Co	<	1 ppm
	Cu	<	1 ppm
	Fe	<	1 ppm
	Mn	<	1 ppm
	Mo	<	2 ppm
	Nb	=	6 ppm
	Ni	<	1 ppm
	P	=	8 ppm
	Pb	<	1 ppm
	Sb	=	2 ppm
	Si	=	17 ppm
	Sn	=	7 ppm
	Sr	<	1 ppm
	Ta	<	1 ppm
	U	<	10 ppm