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GEL PREPARATION OF STARTING MATERIALS FOR  
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A large number of requests for information on the preparation of starting material by the "gel" method have been received in these laboratories over the past few years. In view of this expressed interest we present a brief description of one of a related series of methods of starting material preparation developed principally under the guidance of Dr. R. Roy (1956).

The method is based on the volumetric combination of carefully standardized aqueous solutions of metal nitrates and hydroxides and ludox.<sup>2</sup> This discussion will be limited to gels containing silica, alumina, lime, magnesia, potash and soda, although it can be extended to include other constituents. These six oxides include all the major non-volatile constituents of the igneous and metamorphic rocks with the exception of the oxides of iron.

Table I gives the preferred and an alternate source of the various oxides. The chosen concentrations of the individual solutions will be governed in part by the factors peculiar to a particular investigation, such as the quantity of material required, the composition desired, the permissible limits of error and the solubility of the nitrate salt. In general, the solutions can be standardized with a reproducibility of less than 0.1 weight per cent of the amount present, and the volumetric errors are of the same order of magnitude.

The general procedure for the preparation of the gels is as follows:

Prepare a series of solutions of convenient concentrations. The metal nitrate hydrates of Ca, Mg, and Al are not good weighing forms because of their deliquescent nature, and if they are used the solutions must be carefully standardized. Suggested procedures for standardization of all solutions are as follows:

*SiO<sub>2</sub>*. Evaporate an aliquot to dryness, ignite and weigh. Determine impurity in the residue spectroscopically and by flame photometry. Note that the ludox for this standardization should be dispensed in exactly the same manner as it will in the preparation of

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<sup>2</sup> Ludox is a trade name of the E. I. du Pont de Nemours Company and is a soda or ammonia stabilized silica sol of high purity. The dominant impurities in the ammonia stabilized variety are Na<sub>2</sub>O, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>.

TABLE I. SOURCE OF MATERIAL FOR GEL PREPARATION

Oxide	Preferred Source	Alternate Source
SiO <sub>2</sub>	ludox	tetra-ethyl orthosilicate
Al <sub>2</sub> O <sub>3</sub>	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Al metal
CaO	CaCO <sub>3</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O
MgO	Mg metal	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
K <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	KOH (1 N aqueous)
Na <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	NaOH (1 N aqueous)

the gels. Note further that the alkali content of the ludox will lead to an erroneous value for SiO<sub>2</sub> if the latter is determined by direct treatment of the dried residue with sulfuric and hydrofluoric acids.

*Al<sub>2</sub>O<sub>3</sub>*. Evaporate an aliquot to dryness, ignite and weigh. Determine impurity in the residue spectrographically.

*CaO*. Prepare calcium nitrate solution from reagent grade CaCO<sub>3</sub>, which has been carefully dried and weighed: dissolve in nitric acid, and dilute to volume with distilled and deionized water. If the hydrated nitrate is used the solution must be standardized, for example by EDTA titration, or better gravimetrically by precipitation of calcium oxalate in a suitable aliquot and ignition to CaCO<sub>3</sub> or CaO.

*MgO*. Dissolve pure, cleaned magnesium metal in dilute nitric acid, and dilute to volume with distilled and deionized water. If the hydrated nitrate is used the solution must be standardized, either by EDTA titration, or gravimetrically by double precipitation of magnesium ammonium phosphate, followed by ignition to Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. The latter procedure is more accurate, but is a much more difficult analytical operation than is generally realized, and in unskilled hands frequently gives high values. (Hoffman and Lundell, 1930.) The magnesium pyrophosphate may be examined for extraneous metals (particularly calcium) spectrographically.

*Na<sub>2</sub>O and K<sub>2</sub>O*. Prepare alkali nitrate solutions from reagent grade carbonates which have been carefully dried and weighed: dissolve in nitric acid, and dilute to volume with distilled and deionized water. Alternatively, volumetric standard, CO<sub>2</sub> free, hydroxides commercially available<sup>1</sup> may be used.

Combine the calculated volumes of the standardized solutions in a screw-cap polyethylene container of suitable size, dispensing from a burette. Solutions of lime, magnesia, and alumina should be mixed together first, then treated with sufficient reagent grade nitric acid to prevent precipitation of the metal hydroxides when the alkali and silica solutions are added. Then add the alkali solutions followed by the requisite amount of silica as ludox. During the combination of the various solutions mild agitation should be provided by means of a magnetic stirring device. Depending on the composition of the mixture, it will generally form a gel within a few hours or days.

<sup>1</sup> Hellige, Inc., standardized volumetric concentrates.

After the gel has formed remove the upper portion of the polyethylene container with a razor blade, and cover the resulting container with a watch glass. Desiccate in a 50°–60° C. oven. An enclosure 20×16×19 inches high lined with aluminum foil and containing one 250 watt infrared bulb is satisfactory. If the temperature is allowed to exceed about 70° C., spattering may occur, or too rapid desiccation may produce a non-uniform crust.

Transfer the powder to a silica glass beaker, or a platinum crucible, and heat over a Meker type burner until the evolution of brown nitrogen oxides ceases. Grind the resulting material in agate, transfer to a platinum crucible and heat to decompose the remaining nitrates. Avoid overheating, which may result in partial crystallization or melting, which is usually undesirable. The petrographic microscope and *x*-ray diffraction may be used to advantage for control purposes at this stage. Finally, grind the powder in agate and transfer to a storage vial. The material is extremely hygroscopic and should be stored over anhydrous magnesium perchlorate.

The chief error inherent in this procedure lies in the dispensing of the solutions. It is of utmost importance that the solutions, particularly of alumina and silica, be dispensed during standardization using the same apparatus and technique as in preparing gels.

It is also necessary to consider the soda content of the ludox. For example, the amount of Na<sub>2</sub>O solution calculated for a typical gel was reduced from 20.01 ml to 17.77 ml when the Na<sub>2</sub>O in the added ludox was considered. It is advisable to re-standardize the solutions each time a series of gels is to be prepared.

The precision possible with this method in routine use is indicated in Table II, in which the calculated composition is compared with values resulting from gravimetric analyses. The analyses were performed before any knowledge of the calculated compositions were available to the analyst.

The major discrepancy in the Al<sub>2</sub>O<sub>3</sub> values of 1, 2, 3, 4, and 6, result from the use of different dispensing techniques during the gel preparation and standardization. Sample 5 was prepared using the same burette both for standardization and for dispensing during the preparation of the gels.

For most investigations the volumetric dispensation of the solutions is satisfactory. For maximum precision it is suggested that weight burettes may be used.

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TABLE II. CALCULATED COMPOSITIONS AND GRAVIMETRIC ANALYSES

	1	2	3	4	5	6
Calculated						
SiO <sub>2</sub>	42.50	62.64	57.12	51.49	75.56	61.38
Al <sub>2</sub> O <sub>3</sub>	20.95	16.44	11.86	7.22	14.30	20.89
CaO	—	—	—	—	—	8.22
MgO	17.19	5.73	20.06	34.62	—	—
K <sub>2</sub> O	19.36	15.19	10.96	6.67	4.23	—
Na <sub>2</sub> O	—	—	—	—	5.91	9.51
Total	100.00	100.00	100.00	100.00	100.00	100.00
Gravimetric Analyses						
SiO <sub>2</sub>	42.73	62.64	57.31	51.44	75.40	61.28
Al <sub>2</sub> O <sub>3</sub> <sup>1</sup>	20.34	15.94	11.34	7.10	14.33	20.40
CaO	nd	nd	nd	nd	nd	8.57
MgO	17.23	5.83	20.10	34.64	nd	nd
K <sub>2</sub> O	19.41	15.26	11.01	6.65	4.27	nd
Na <sub>2</sub> O	0.14	0.20	0.15	0.13	5.92	9.48
H <sub>2</sub> O	0.07	0.07	0.06	0.04	0.00	nd
Total	99.92	99.94	99.97	100.00	99.92	99.73

<sup>1</sup> Includes Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, etc.

SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO were determined by classical gravimetric procedures. Na<sub>2</sub>O and K<sub>2</sub>O were weighed as chlorides after a J. Lawrence Smith Separation, and K<sub>2</sub>O was weighed as chloroplatinate. After conversion of the chloroplatinates of sodium and potassium to sulfates and weighing, Na in the K fraction and K in the Na fraction were determined by flame photometry. Li, Rb and Cs were found in only inappreciable amounts.

this technique are gratefully acknowledged. The method described in this report has been used to prepare a large number of starting materials for use in studies financially supported by the National Science Foundation.

#### REFERENCES

- HOFFMAN, J. I. AND G. E. F. LUNDELL (1930) The precipitation and ignition of magnesium ammonium phosphate. *Natl. Bur. Stand., Jour. Res., Res. Paper* **200**, 279.
- ROY, R. (1956) Aids in hydrothermal experimentation: II. Methods of making mixtures for both "dry" and "wet" phase equilibrium studies. *Jour. Am. Ceram. Soc.* **39**, 145.