

The SPEX Speaker

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PREPARATION OF STANDARDS FOR PLASMA EMISSION SPECTROSCOPY

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Plasma emission spectroscopy, combining the precision and accuracy of atomic absorption with the multielement capabilities of dc arc and spark emission spectroscopy, has justifiably experienced a phenomenally rapid growth over the last few years. Offering lower detection limits and fewer matrix effects, both ICP and DCP have found wide application in as diversified an array of fields as water quality testing, soil analysis, biological screening, geological surveys, metals analysis, and a host of others.

As with any instrumental method, the quality of the data can be only as good as that of the standards from which the instrument is calibrated. And the preparation of these essential, very pure, highly accurate, single-element or multielement standards for plasma emission is a formidable task.

In emission spectroscopy the determination of trace contaminants in high purity materials requires a series of dilution standards which must be made from a spectrographically pure base that will provide a sufficiently low blank. Similarly, in AA analyses a pure matrix material is spiked with various levels of the impurity which is being determined in order to match the matrix of the sample and standards. In plasma emission analyses, however, the purity of the base material is even more important because of the generally lower detection limits cited in Table 1.

It is readily apparent from the data that if one were preparing standards for dc-arc analysis of traces of iron in a compound, a base material containing 1 ppm of Fe would be quite adequate while for the plasma method, the detection limit is roughly three orders of magnitude less and would, therefore, require a purer standard if one were looking for Fe in the ppb range.

Another application of very pure single element standards is the determination of spectral interferences on multi-channel ICP and DCP spectrometers.

Normally, a solution of a pure element is aspirated into the plasma and the effect of the emission on the channels of all other elements is measured to obtain correction factors for the computer. The signal observed in each channel must be due to spectral interference and not measurable concentrations of an impurity element.

Having established the importance of a low blank, let us evaluate all factors which contribute impurities to the standard. The major ingredient, water, like most reagents, is available in several purities. Tap water usually contains large quantities of Na, Ca, and Mg along with lower levels of Si, organics and colloids. Distillation tends to remove a large part of dissolved solids, and reduces metallic contamination; however, some particulates can be carried over in the distillate, as can volatile organometallics or steam distillable compounds such as H_3BO_3 .

Deionized water is somewhat better, and with two cartridges in series, water approaching theoretical resistivity of 18 megohm cm^{-1} can be achieved. The conductivity can be deceiving, however, since neutral species, organometallics, and colloidal metal oxides or hydroxides can still be present. A combination of purification processes is best and several commercial units are marketed. Both Barnstead's and Millipore's water purification systems include a reverse-osmosis cartridge, to prepurify the

TABLE I
ESTIMATED DETECTION LIMITS
OF MAJOR SPECTROSCOPIC METHODS

| ELEMENT | ICP - AES [1,2] (ppm) | FLAME - AAS [3] (ppm) | D.C. ARC - OES [4] (ppm) |
|---------|--------------------------|-----------------------------|--------------------------------|
| Al | .005 | .02 | 5 |
| As | .015 | .1 | 50 |
| Cd | .0005 | .001 | 10 |
| Ca | .0005 | .005 | .2 |
| Cu | .0005 | .003 | .5 |
| Fe | .001 | .005 | 2 |
| Pb | .01 | .015 | 5 |
| Mg | .00005 | .0005 | .2 |
| Mn | .001 | .020 | 1 |
| P | .025 | 25 | 50 |
| K | .25 | .001 | 1000 |
| Si | .010 | .060 | .5 |
| Na | .025 | .0005 | 500 |
| Zn | .0002 | .001 | 10 |

TABLE II
COMPARISON OF LABORATORY WATER QUALITY [5]

| SPECIFICATION | TYPICAL TAP WATER | SINGLE DISTILLED | SINGLE DEIONIZED (A.S.T.M. TYPE III) | MULTIPLE DEIONIZED (MEGOHM, A.S.T.M. I) |
|--|-----------------------------|---------------------|---|--|
| Specific Resistance (For total ionic content) | 0.001- 0.005 Mohms/cm | 0.05- 0.5 | 0.2- 1.0 | 10- 18 |
| Total Matter (mg/l) (For non-ionics colloids, organometals.) | 200- 500 ppm | 6- 10 | 1- 2 | 0.01- 0.1 |
| Silicates (mg/l) | 1- 10 ppm | 1- 2 | 0.1- 0.7 | <0.01 |
| Heavy Metals (mg/l) | 10- 100 ppm | 1- 5 | 0.1- 0.8 | <0.01 |
| Sodium (mg/l) | 50 200 ppm | 5- 10 | 0.5- 1.0 | <0.1 |
| Hardness (mg/l) (Includes Ca, Mg & Some Trans. Mets.) | 25 100 ppm | 1- 5 | 0.05- 0.1 | None Detected |

water, followed by a charcoal filter to remove organics and organometallics. The water then passes through two ion-exchange cartridges to remove ionic compounds, and finally through a double .22 micron filter to remove colloids and traces of ion exchange resins. A summary of the impurities in various types of water is given in Table II.

In addition to the water, any acids added to the solution, especially at high concentrations, can contribute significant contamination. Table III presents a summary of the typical impurities in various types of commercial acids. It can readily be seen that there is a considerable difference between reagent grade and ultra pure acids. It should be pointed out, however, that there is no advantage to the highest purity acids if they are not opened in a clean room environment, so for most laboratories an electronic grade acid is adequate.

The most important ingredient in the standard is the major element which can be added by dissolving the metal directly or by preparing a solution from an oxide, carbonate, or a salt. As the concentration of the element is increased from 100-10,000 ppm in the standard, the purity requirements become increasingly stringent. Reagent grade compounds are generally unsuitable for the preparation of any high purity standards for plasma emission methods, except for routine calibration of single channel instruments in quality control work. Much higher purity metals can be obtained by zone refining or wet chemical purifications. Such techniques for purifying metal compounds include ion exchange chromatography, solvent extraction, recrystallization, selective precipitation, and sublimation, to name a few. For comparison, several cobalt standard solutions were prepared from commercial grades of Co and various purified grades of Co compounds. The results are summarized in Table IV.

It is readily apparent that the primary producer grade of Co metal and reagent $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are heavily contaminated with other Group VIII metals, Fe and Ni. By passing the Co solution through a Dowex-1-X8 anion exchange resin in 9M HCl, elements such as Fe and Zn are adsorbed on the resin as anionic chloro-complexes along with the Co while alkali and alkaline earth metals are eluted along with cationic aquo complexes of Ni, and Mn. The Co can then be eluted selectively with 4M HCl which converts it to the cationic hexaquo species.

As an alternative, unlike its major impurities, Co can be oxidized to Co(III) which forms many inert complexes.

TABLE III
ANALYSIS OF ACIDS FOR SAMPLE AND STANDARD PREPARATION

| IMPURITY (In ppb) | A.C.S. REAGENT GRADE | | ELECTRONIC GRADE | | VYCOR REDISTILLED | |
|------------------------|-------------------------|----------------|---------------------|----------------|----------------------|----------------|
| | HCl | HNO_3 | HCl | HNO_3 | HCl | HNO_3 |
| Arsenic (As) | 1000 | 50 | 25 | 1 | 10 | 1 |
| Iron (Fe) | 1000 | 250 | 100 | 50 | 25 | 10 |
| Heavy Metals | 2000 | 500 | 250 | 50 | 100 | 25 |
| Residue (Ash, Alkalis) | 5000 | 5000 | 250 | 100 | — | 100 |
| Copper (Cu) | 500 | 100 | — | — | — | — |
| Total Sulfur | 2000 | — | 500 | 20(P) | 200 | — |

TABLE IV
PARTS PER MILLION IMPURITIES IN VARIOUS 100,000 PPM Co STANDARDS IN ~20% HCl

| Impurity Element | Co Metal | Reagent $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ | $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ Purified By Ion Exchange | Recryst. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ | Sublimed* CoCl_2 |
|------------------|----------|---|--|--|---------------------------|
| Fe | 677 | 787 | 17 | 20 | — |
| Ni | 51 | 78 | <3.7 | <.01ND | <.1ND |
| Zn | 10.4 | 2.7 | .4 | .5 | <.1ND |

Analysis performed by Dr. A. Zander, Spectrametrics, Inc., Andover, Massachusetts
* concentration is 10,000 ppm Co in 20% HCl; detection limit normalized to 100,000 ppm Co

The Co(III) amine complexes can be recrystallized from HCl as a cationic complex while the labile Ni and Fe form anionic chloro-complexes; conversion to CoCl_2 followed by sublimation may further reduce impurity levels.

Although these examples are specific for Co, a study of the literature generally reveals several methods for purifying each element, the choice of which is usually dictated by the impurities present in a given lot of material.

The final factor to be considered in maximizing the purity of a plasma emission standard is the choice of container. Several excellent articles exist on the leaching of impurities from various organic polymer containers [6]. In general, conventional polyethylene and Teflon appear to be the best choices and have minimal losses of water after sitting on the shelf for extended periods of time. For CPE, leaching with 1:1 HNO_3 for one week appears to be the preferred cleaning method for most elements, and an HNO_3 wash rather than HCl also eliminates the possibility of any adsorbed Cl in the plastic which could precipitate out elements such as Ag in a multielement mixture.

While each of the factors described above is important, their cumulative effect is even more significant. Table V shows a comparison of the impurity levels in two hypothetical standards. One is prepared from reagent grade chemicals and acids, and singly distilled

water in an unleached bottle; the other is prepared from the highest quality water, electronic grade acids, and spectrographically pure compounds in a preleached bottle.

The results clearly indicate positive errors ranging from ~.1 to 3% of the value of the major element. Certainly a sodium standard labeled 1000 $\mu\text{g}/\text{ml}$ which actually contains 1030 $\mu\text{g}/\text{ml}$ is unacceptable for any work requiring a high degree of accuracy.

The purity aspect of the standard is only one side of the coin. Many manufacturers of ICP and DCP instrumentation claim results with accuracies of $\pm 1\%$ under favorable conditions, which approach the accuracy of many wet methods, especially for difficult-to-determine elements in complex mixtures. It is, therefore, essential that the calibration of the standard used in the analysis be considerably better than $\pm 1\%$.

Several publications have appeared in the last few years which recommend various starting materials for the preparation of standards for ICP and DCP methods and their pretreatment prior to dissolution [7,8,9]. While much of the information is helpful to the chemist, if one is not careful, gross errors can be encountered by assuming a compound is stoichiometric, even after it has been dried at 110°C or ignited at high temperature.

TABLE V

COMPARISON OF CONTRIBUTED IMPURITIES IN A HYPOTHETICAL STANDARD PREPARED FROM REAGENT GRADE AND ULTRA-PURE MATERIALS (15 ELEMENTS AT 1000 PPM EACH IN 10% HCl)

| ELEMENT | MATERIALS* | | ACID | | WATER | | STORAGE | | TOTAL | |
|--|------------|------------|---------|--------|-----------|--------|---------|---------|----------|------------|
| | Reagent | Ultra-Pure | Reagent | Elect. | Distilled | D.D.I. | Unclean | Cleaned | Reagent | Ultra-Pure |
| As | 3500 ppb | 20 ppb | 10 | 0.2 | | 0.05 | | | 3510 ppb | 20.3 ppb |
| Ca | 15,000 | 150 | | 2 | 0.2 | 0.02 | 100 | | 15,100 | 152 |
| Cu | 1500 | 25 | | 0.2 | 1.2 | 0.05 | 10 | | 1512 | 25.3 |
| Fe | 3500 | 100 | 100 | 1 | 2 | 0.02 | 50 | | 3652 | 101 |
| Pb | 3000 | 30 | 200 | 0.1 | 0.1 | 0.008 | 20 | | 3220 | 31 |
| Mg | 13,500 | 50 | | 0.5 | 0.5 | 0.03 | 10 | | 13,511 | 51 |
| Mn | 500 | 25 | | | 0.3 | 0.01 | | | 501 | 25 |
| K | 15,000 | 20 | | | 2 | 0.05 | 5 | | 15,007 | 20.1 |
| Na | 30,000 | 50 | | | 5 | 0.07 | 50 | | 30,055 | 51 |
| Si | 2000 | 100 | | 2 | | 0.5 | | | 2000 | 103 |
| Ag | — | — | | | 5 | 0.01 | 5 | | 10 | 0.01 |
| R ₂ O ₃ (Al,Cr) | 5000 | 50 | | | | 0.5 | 25 | | 5025 | 51 |
| Zn | 4500 | 20 | | 0.1 | 0.2 | 0.03 | 10 | | 4511 | 20.1 |

*NOT INCLUDING 1000 PPM OF ELEMENT IN STANDARD.

*ALL IMPURITY VALUES ARE BASED ON MANUFACTURER'S SPECIFICATIONS

Materials such as basic beryllium acetate, boric acid, or selenous acid cannot be dried without partial decomposition, which will raise the % metal in the compounds by a considerable amount. Hydrates are generally a poor choice of starting materials since the water content may vary considerably from one lot to another and most are hygroscopic. Oxides are more stable. However, some such as Co₃O₄, MnO₂ and Pr₆O₁₁ are non-stoichiometric, while others such as MgO absorb CO₂ and H₂O from the air, sometimes irreversibly. Furthermore, many oxides may be soluble in one acid but not another. Metals may be dissolved directly to prepared standards; however, care must be taken when using HCl if the halides are volatile. For example, Ge will dissolve in aqua-regia; however, much will be lost as volatile GeCl₄, leading to a large negative error.

As an illustration of the variability in the assay of various types of materials,

several batches of commercial compounds were analyzed by wet chemical methods. Table VI clearly shows that one cannot assume a theoretical % metal in a compound without introducing errors as high as 50%.

In another experiment, a sample of untreated La₂O₃ was analyzed 1) off the shelf, 2) after drying at 110C to remove H₂O, 3) after ignition at 1000C to remove CO₂ and, finally, 4) at the end of a three-day period during which the ignited sample sat in an open dish. The results are summarized in Table VII. It is interesting that even after ignition at 1000C the assay did not equal the theoretical value. This is most likely due to incomplete loss of CO₂, which is not surprising since some carbonates, e.g., BaCO₃, are stable to 1450C. Furthermore, reabsorption of CO₂ results in a constantly decreasing assay. It is, therefore, imperative for accurate standards that each material be assayed by an accurate wet chemical method for the

exact metal content before dissolution. In single element standards, analysis of the resulting solution is also recommended.

Once the solution is prepared, its stability must also be considered. In a single element solution, interaction with the container can result in precipitate formation. Materials in the polymer can act as reducing agents and result in plating out of certain elements such as Se or Au on the container walls. This problem can be eliminated by soaking the bottles for several days in concentrated nitric acid before introducing the standard.

In porous plastic containers, HCl fumes tend to diffuse through the container walls, resulting in a gradual diminishing of the acid concentration inside the container. This can lead to eventual precipitation of easily hydrolyzed halides of such metals as Ta, Nb, Sb, Ti and Sn. Standards prepared from the latter two elements appear to be stable in HCl when the standard is made from dissolution of the metal since Ti⁺³ and Sn⁺² are present initially. Slow oxidation on the shelf, however, gives Ti⁺⁴ and Sn⁺⁴ which are considerably more hydrolyzed and, in dilute HCl, tend to precipitate from solution. Hydrolysis, of course, can be prevented by storing these standards in pre-leached glass bottles, since HCl will not diffuse through their walls.

In very dilute solutions, some elements tend to adsorb on the container walls and reduce the shelf life of the standard. An excellent review of the stability of trace elements in plastic containers under various conditions is available [10].

TABLE VI

ERRORS IN STOICHIOMETRY OF SUGGESTED STARTING MATERIALS

| COMPOUND | THEORETICAL ASSAY | ANALYZED RANGE | |
|--|--------------------|----------------|--------|
| | | (Low) | (High) |
| Na ₂ SiO ₃ ·9H ₂ O (Wide Hydration Range) | 9.88% Si | 8.3% | 16.5% |
| Ca(NO ₃) ₂ ·3H ₂ O & (.4H ₂ O) (Several Stable Hydrates Exist) | 18.37% (16.97%) Ca | 15.8% | 20.2% |
| LaCl ₃ ·6H ₂ O & (.7H ₂ O) (Various Hydrate Modifications) | 39.31% (37.40%) La | 36.2% | 42.0% |
| MgO (Absorbs CO ₂ & H ₂ O Readily) | 60.32% Mg | 57.3% | 60.3% |
| MnO ₂ (Variable Oxid; Non-Stoich.) Also Mn ₂ O ₃ =69.60%, Mn ₃ O ₄ =72.03% | 63.19% Mn | 62.0% | 65.8% |
| Co ₂ O ₃ (Variable Oxid., Non-Stoich.) Also Co ₃ O ₄ =73.43% | 71.06% Co | 69.2% | 72.7% |
| Pr ₆ O ₁₁ (Variable Oxid., Non-Stoich.) Also PrO ₂ =81.49%, Pr ₂ O ₃ =85.45% | 82.77% Pr | 81.1% | 83.2% |

TABLE VII
ANALYSIS OF La_2O_3 AFTER VARIOUS PRE-TREATMENT

| | La_2O_3 % | La % |
|---|---------------------------|-------|
| Theoretical | 100 | 85.27 |
| Typical Bulk Sample (Air equilibrated) | 98.0 | 83.6 |
| Sample dried at 110C (Moisture removed) | 98. | 84.0 |
| Sample ignited at 1000C (Decomposition of OH^- and CO_3^{2-}) | 99.5 | 84.8 |
| Sample re-equilibrated (72 hrs, uptake of CO_2 and H_2O) | 98.3 | 83.8 |

In the case of multielement mixtures, the problems become much more complex. Everyone assumes that AgCl is insoluble in water; however, in concentrated HCl , Ag levels in excess of 50 ppm are stable due to formation of AgCl_2^- ion. It is, therefore, possible to prepare multielement solutions containing Ag in an HCl matrix if the concentration is sufficiently low. On the other hand, some salts which are very soluble in water become much less soluble in concentrated acids, so that while it is no problem preparing 10,000 ppm solutions of Ba or Pb nitrate in water, the nitrates precipitate out of concentrated HNO_3 solutions.

Elements such as W , Si , Mo , Nb , and Ta present additional problems in multielement solutions because their solubility is very dependent upon the matrix. In various attempts to keep Si in solution in several different multielement

mixtures, we have had to resort to compounds such as ammonium salt of trimethylsilylpropionic acid, silicotungstic acid, and cesium metasilicate as well as the more common ammonium hexafluorosilicate, or sodium silicate.

While solutions appear to be stable when freshly prepared, various combinations of elements can result in the formation of precipitates on the shelf, sometimes very quickly and other times over a period of months depending upon the elements and their concentrations. Spectrographic analysis of precipitates which have formed in several multielement solutions have taught us the hard way that calcium vanadate, lead molybdate, and barium selenite are not soluble in dilute HCl at the 1000 ppm level.

For those who like crossword puzzles,

the preparation of multielement solutions is an even greater challenge. Just as one thinks he has all of the possible interelement interactions solved, someone requests a new combination of elements, all in one solution, naturally, and the search begins once again for the right combinations of compounds and matrix which will give a stable standard. Happiness is a clear, long-lasting, multielement solution standard!

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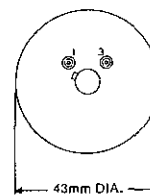
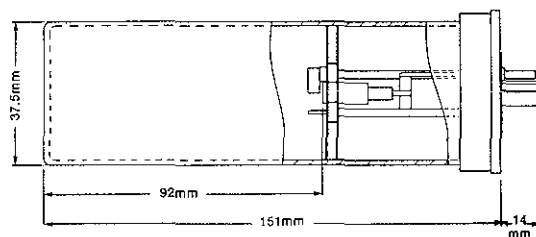
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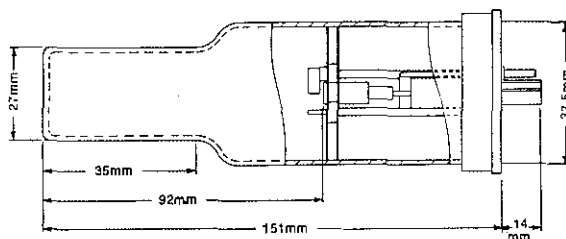
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| Beryllium | 3QNY-110D | 15 | 175. | Phosphorus | 3QNY-182C | 10 | 200. |
| Bismuth | 3QAY-112B | 6 | 145. | Platinum | 3QNY-184C | 15 | 150. |
| Boron | 3QNY-114D | 12 | 150. | Potassium | 3BNX-186C | 8 | 150. |
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| Calcium | 3UNX-118C | 6 | 120. | Rhenium | 3UAX-190C | 15 | 190. |
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| Erbium | 3BNX-134C | 15 | 186. | Silicon | 3QNY-1104D | 15 | 140. |
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| Gold | 3QNY-144C | 10 | 150. | Tellurium | 3QNY-1114B | 6 | 181. |
| Hafnium | 3UAX-146C | 15 | 181. | Terbium | 3BNX-1116C | 15 | 186. |
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| Lanthanum | 3UAX-156B | 15 | 175. | Titanium | 3UNX-1126C | 15 | 120. |
| Lead | 3QNY-158C | 6 | 120. | Tungsten | 3QNY-1128C | 15 | 140. |
| Lithium | 3BAX-160C | 10 | 130. | Uranium | 3UAX-1130C | 15 | 210. |
| Lutetium | 3UAX-162D | 8 | 200. | Vanadium | 3UNX-1132D | 15 | 150. |
| Magnesium | 3QNY-164B | 4 | 120. | Ytterbium | 3UNX-1134D | 15 | 186. |
| Manganese | 3UAX-166D | 12 | 120. | Yttrium | 3BNX-1136C | 15 | 186. |
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| + Iron | 3QNY-208C | 10 | 165. |
| + Manganese | 3QNY-210C | 10 | 165. |
| + Nickel | 3QNY-212C | 10 | 165. |
| Cobalt + Copper | 3QNY-214C | 10 | 165. |
| + Iron | 3QNY-216C | 10 | 165. |
| + Manganese | 3QNY-218C | 10 | 165. |
| + Nickel | 3QNY-220C | 10 | 165. |
| Copper + Iron | 3QNY-222C | 10 | 165. |
| + Manganese | 3QNY-224C | 10 | 165. |
| + Nickel | 3QNY-226C | 10 | 165. |
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| + Nickel | 3QNY-232C | 10 | 165. |
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| Element | | Cat. No. | Max. mA | Price \$ |
|-----------------------|-------------|-----------|------------|----------|
| Three Elements | | | | |
| Chromium+Cobalt | + Copper | 3QNY-302C | 10 | 140. |
| | + Iron | 3QNY-304C | 10 | 140. |
| | + Manganese | 3QNY-306C | 10 | 140. |
| | + Nickel | 3QNY-308C | 10 | 140. |
| Chromium+Copper | + Iron | 3QNY-310C | 10 | 140. |
| | + Manganese | 3QNY-312C | 10 | 140. |
| | + Nickel | 3QNY-314C | 10 | 140. |
| Chromium+Iron | + Manganese | 3QNY-316C | 10 | 140. |
| | + Nickel | 3QNY-318C | 10 | 140. |
| Chromium+Manganese | + Nickel | 3QNY-320C | 10 | 140. |
| Cobalt+Copper | + Iron | 3QNY-322C | 10 | 140. |
| | + Manganese | 3QNY-324C | 10 | 140. |
| | + Nickel | 3QNY-326C | 10 | 140. |
| Cobalt+Manganese | + Nickel | 3QNY-328C | 10 | 140. |
| Copper+Iron | + Manganese | 3QNY-330C | 10 | 140. |
| | + Nickel | 3QNY-332C | 10 | 140. |
| Copper+Manganese | + Nickel | 3QNY-334C | 10 | 140. |
| Iron+Manganese | + Nickel | 3QNY-336C | 10 | 140. |

Four Elements

| | | | | |
|---------------------------|-------------|-----------|----|------|
| Chromium+Cobalt+Copper | + Iron | 3QNY-402C | 10 | 151. |
| | + Manganese | 3QNY-404C | 10 | 151. |
| | + Nickel | 3QNY-406C | 10 | 151. |
| Chromium+Cobalt+Iron | + Manganese | 3QNY-408C | 10 | 151. |
| | + Nickel | 3QNY-410C | 10 | 151. |
| Chromium+Cobalt+Manganese | + Nickel | 3QNY-412C | 10 | 151. |
| Chromium+Copper+Iron | + Manganese | 3QNY-414C | 10 | 151. |
| | + Nickel | 3QNY-416C | 10 | 151. |
| Chromium+Copper+Manganese | + Nickel | 3QNY-418C | 10 | 151. |
| Chromium+Iron+Manganese | + Nickel | 3QNY-420C | 10 | 151. |
| Cobalt+Copper+Iron | + Manganese | 3QNY-422C | 10 | 151. |
| | + Nickel | 3QNY-424C | 10 | 151. |
| Cobalt+Copper+Manganese | + Nickel | 3QNY-426C | 10 | 151. |
| Cobalt+Iron+Manganese | + Nickel | 3QNY-428C | 10 | 151. |
| Copper+Iron+Manganese | + Nickel | 3QNY-430C | 10 | 151. |

Five Elements

| | | | | |
|---|--|-----------|----|------|
| Chromium+Cobalt+Copper+Iron+Manganese | | 3QNY-502C | 10 | 161. |
| Chromium+Cobalt+Copper+Iron+Nickel | | 3QNY-504C | 10 | 161. |
| Chromium+Cobalt+Copper+Manganese+Nickel | | 3QNY-506C | 10 | 161. |
| Chromium+Cobalt+Iron+Manganese+Nickel | | 3QNY-508C | 10 | 161. |
| Chromium+Copper+Iron+Manganese+Nickel | | 3QNY-510C | 10 | 161. |
| Cobalt+Copper+Iron+Manganese+Nickel | | 3QNY-512C | 10 | 161. |

Six Elements

| | | | |
|--|-----------|----|------|
| Chromium+Cobalt+Copper+Iron+Manganese+Nickel | 3QNY-602C | 10 | 175. |
|--|-----------|----|------|

NEW HIGH PURE MATERIALS.....

The following 18 compounds supplement our 25th anniversary catalog listing offered in July, 1979. In addition to pricing information, a disposal procedure key (DP) and shipping restrictions (DOT) are indicated.

These additions are primarily a response to customer request; their applications are widespread and include standards for density gradient ultracentrifugation, Cs31, Cs85; and a hydrogenation catalyst Pt45. In addition, new water soluble compounds are listed for preparing aqueous solution standards in neutral solution without hydrolysis, Sb70, Ge50, and Fe20, as well as a primary standard for EDTA titrations, Zn20.

| CAT NO | COMPOUND | FW | FORM | DP | DOT | TMI MAX ppm | QTY grams | PRICE US\$ |
|--------|---|---------|--------|-----|-----|----------------|--------------|---------------|
| AL95 | SODIUM HEXAFLUOROALUMINATE Na_3AlF_6 synthetic cryolite | 209.95 | powder | 11 | | 50 | 50 | 45.00 |
| | | | | | | | 250 | 180.00 |
| SB70 | POTASSIUM ANTIMONYL TARTRATE $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ water soluble, stable antimony compound for preparation of aqueous standards | 333.94 | powder | 27d | | 50 | 25 | 35.00 |
| | | | | | | | 125 | 140.00 |
| C080 | COBALT TETRATHIOCYANATOMERCURATE (II) $\text{Co}[\text{Hg}(\text{SCN})_4]$ suitable for calibration of a magnetic susceptibility balance | 491.84 | powder | 27b | | 100 | 10 | 35.00 |
| | | | | | | | 50 | 140.00 |
| CS31 | CESIUM CHLORIDE CsCl suitable for density gradient ultracentrifugation Abs. of 1 cm of a 50% soln. at 260 nm <.02 | 168.36 | powder | 11 | | 5 | 20 | 19.00 |
| | | | | | | | 100 | 76.00 |
| | | | | | | | 1000 | 300.00 |
| CS85 | CESIUM SULFATE Cs_2SO_4 suitable for density gradient ultracentrifugation Abs. of 1 cm of a 50% soln. at 260 nm <.02 | 361.87 | powder | 11 | | 5 | 20 | 24.00 |
| | | | | | | | 100 | 96.00 |
| | | | | | | | 1000 | 390.00 |
| CU12 | AMMONIUM TETRACHLOROCUPRATE (II) $(\text{NH}_4)_2\text{CuCl}_4$ | 241.42 | powder | 27k | | 5 | 20 | 35.00 |
| | | | | | | | 100 | 140.00 |
| G047 | GADOLINIUM GALLIUM GARNET (GGG) $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ | 1012.34 | powder | 26 | | 100 | 25 | 50.00 |
| | | | | | | | 125 | 200.00 |

... ADDITIONS TO OUR 1979 25th ANNIVERSARY CATALOG

| CAT NO | COMPOUND | FW | FORM | DP | DOT | TMI MAX ppm | QTY grams | PRICE US\$ |
|--------|---|--------|----------|-----|-----|----------------|--------------|-----------------|
| GE50 | AMMONIUM TRISOXALATOGERMANATE (NH ₄) ₂ Ge(C ₂ O ₄) ₃ ·4H ₂ O water soluble, stable Ge compound useful for preparing aqueous standards | 444.77 | powder | 27k | | 20 | 10 50 | 45.00 180.00 |
| FE20 | AMMONIUM TRISOXALATOFERRATE (NH ₄) ₃ Fe(C ₂ O ₄) ₃ ·3H ₂ O water soluble, stable Ge compound for preparation of aqueous standards | 428.07 | powder | 11 | | 10 | 50 250 | 45.00 180.00 |
| PB80 | LEAD OXIDE Pb ₃ O ₄ | 685.57 | powder | 27f | | 10 | 25 125 | 40.00 160.00 |
| LI72 | LITHIUM NIOBATE LiNbO ₃ | 147.85 | powder | 27k | | 50 | 50 250 | 55.00 220.00 |
| MG30 | MAGNESIUM CARBONATE (BASIC) MgCO ₃ ·XMg(OH) ₂ | | powder | 11 | | 100 | 100 500 | 30.00 120.00 |
| MO35 | CALCIUM MOLYBDATE CaMoO ₄ Powellite | 200.01 | powder | 11 | | 20 | 20 100 | 48.00 192.00 |
| PT45 | PLATINUM DIOXIDE PtO ₂ ·H ₂ O Adam's Catalyst | 227.03 | powder | 27a | | 100 | 1 5 | 42.00 168.00 |
| S75 | AMMONIUM SULFITE (NH ₄) ₂ SO ₃ ·H ₂ O | 134.15 | crystals | 12a | | 10 | 100 500 | 25.00 100.00 |
| SN70 | TIN (II) OXIDE SnO | 134.69 | powder | 26 | | 100 | 50 250 | 25.00 100.00 |
| W30 | CALCIUM TUNGSTATE CaWO ₄ Scheelite | 287.93 | powder | 11 | | 20 | 25 125 | 45.00 180.00 |
| ZN20 | DITHIOCYANATODIPYRIDINE ZINC (II) Zn(C ₅ H ₅ N) ₂ (SCN) ₂ suitable as a primary standard for EDTA solutions | 339.74 | powder | 11 | | 10 | 25 125 | 25.00 100.00 |

SPEX HiPURE BORATE FUSION FLUXES

Fluxing has emerged as the preferred pre-treatment for analyzing intransigent or inhomogeneous substances. For x-ray spectroscopy almost any material can be fused with an appropriate flux. Subsequently the sample is analyzed as a cast disc. For AA, DCP, and ICP, where the sample must be in the liquid state, the substance, once fluxed, can usually be dissolved in a mineral acid. Although lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) is almost universally applicable as a flux, certain mixtures have proved more satisfactory for various reasons.

Generally speaking, acidic fluxes (those rich in lithium tetraborate) are best suited for dissolving basic oxides such as Al_2O_3 or alkali and alkaline earth oxides or carbonates. Lithium meta-

borate (LiBO_2), on the other hand, is more basic, better suited for dissolving acidic oxides such as SiO_2 or TiO_2 .

Another factor to consider is the melting point. The lowest melting flux capable of reacting completely with a sample is usually the optimum flux. Accordingly, mixtures of lithium tetraborate, with the metaborate, or carbonate are often selected. Not only does the low temperature reduce preparation time, it also inhibits the loss of volatile elements.

At the opposite extreme are materials which demand the highest temperatures for total fusing with the flux. ZrO_2 is such an example, requiring a temperature in excess of 1000C.

Most spectroscopic techniques often pose another requirement: inclusion of an element not found in the sample to serve as an internal standard. X-ray spectroscopy often goes further, specifying the addition of a heavy element as an absorber to suppress matrix effects. Then, too, a wetting agent is frequently needed to reduce the tendency of the molten fused mixture to adhere to the walls of the crucible. Frequently all of these requirements can be combined in a single compound such as Spex HiPure bromides or iodides.

The following list of fluxes includes those that we regularly stock. Should you wish to discuss special compounds, mixtures, or preweighs, we shall be glad to have you contact us.

| <u>CAT. NO.</u> | | <u>APPROX.</u> <u>°C M.P.</u> | <u>MAX</u> <u>TMI</u> | <u>QTY</u> <u>LBS.</u> | <u>PRICE</u> |
|-----------------|---|----------------------------------|--------------------------|---------------------------|-----------------|
| LI70 | Lithium Metaborate | 920 | 100 | 1 | \$26.50 |
| LI95 | Lithium Tetraborate | 845 | 100 | 1 10 | 26.50 217.50 |
| NA90 | Sodium Tetraborate | 741 | 10 | 1 | 33.00 |
| FF04 | 90% Lithium Tetraborate/10% Lithium Carbonate | 850 | 50 | 1 10 | 40.00 320.00 |
| FF08 | 80% Lithium Tetraborate/20% Lithium Metaborate | 840 | 50 | 1 10 | 43.00 344.00 |
| FF12 | 67% Lithium Tetraborate/33% Lithium Metaborate | 875 | 50 | 1 10 | 46.00 368.00 |
| FF16 | 50% Lithium Tetraborate/50% Lithium Metaborate | 870 | 50 | 1 10 | 50.00 400.00 |
| FF20 | 90% Lithium Tetraborate/10% Lithium Fluoride | 790 | 50 | 1 10 | 45.00 360.00 |
| FF24 | 80% Lithium Tetraborate/20% Lithium Fluoride | 780 | 50 | 1 10 | 45.00 360.00 |
| FF28 | 80% Lithium Tetraborate/20% Lanthanum Oxide | 900 | 50 | 1 10 | 70.00 560.00 |
| FF32 | 47% Lithium Tetraborate/37% Lithium Carbonate/ 16% Lanthanum Oxide | 700 | 50 | 1 10 | 52.50 420.00 |
| FF36 | 83% Sodium Tetraborate/17% Lanthanum Oxide | 740 | 50 | 1 10 | 50.00 400.00 |

NEW EXPANDED LIST

ORGANIC-SOLVENT-SOLUBLE METAL COMPOUNDS

These metal compounds, soluble in many types of organic solvents, are prepared from SPEX HiPure starting materials to minimize metallic impurities. Each lot is assayed and the exact percentage of metal content is certified on the label.

Ideal for any application requiring a metal compound soluble in non-aqueous media, these materials are particularly helpful in determining traces of wear metals in crude as well as used lubricating oils, food fats and oils, and as standards for x-ray fluorescence analyses of non-aqueous samples.

We also invite your inquiries about any custom compounds including organometallics, coordination compounds, or other salts soluble in organic solvents.

Group I Compounds

| Cat. No. | % | Metal | Salt |
|----------|------|------------|--------------------------------------|
| OAL | 5.6 | Aluminum | Aluminum 2-ethylhexanoate |
| OAS | 12.5 | Arsenic | Arsenic (V) 2-ethylhexanoate |
| OBA | 27.7 | Barium | Barium 4-cyclohexanebutyrate |
| OBI | 32.4 | Bismuth | Bismuth 2-ethylhexanoate |
| OCD | 23.9 | Cadmium | Cadmium 4-cyclohexanebutyrate |
| OCA | 8.4 | Calcium | Calcium 4-cyclohexanebutyrate |
| OCO | 16.3 | Cobalt | Cobalt (II) 4-cyclohexanebutyrate |
| OCU | 16.4 | Copper | Copper (II) 4-cyclohexanebutyrate |
| OLA | 20.8 | Lanthanum | Lanthanum Decanoate |
| OPB | 36.2 | Lead | Lead 4-cyclohexanebutyrate |
| OLI | 3.8 | Lithium | Lithium 4-cyclohexanebutyrate |
| OMG | 6.5 | Magnesium | Magnesium 4-cyclohexanebutyrate |
| OMN | 13.8 | Manganese | Manganese (II) 4-cyclohexanebutyrate |
| OMO | 23.0 | Molybdenum | Molybdenyloxinate |
| ONI | 15.6 | Nickel | Nickel 4-cyclohexanebutyrate |
| OP | 9.1 | Phosphorus | Triphenyl Phosphate |
| OK | 16.6 | Potassium | Potassium 4-cyclohexanebutyrate |
| OSI | 14.0 | Silicon | Octaphenylcyclotetrasiloxane |
| OAG | 37.9 | Silver | Silver 4-cyclohexanebutyrate |
| ONA | 11.8 | Sodium | Sodium 4-cyclohexanebutyrate |
| OSR | 19.7 | Strontium | Strontium 4-cyclohexanebutyrate |
| OTH | 36.5 | Thorium | Thorium 2,4-pentanedionate |
| OSN | 21.5 | Tin | Dibutyltin Bis 2-ethylhexanoate |
| OTI | 13.6 | Titanium | Titanylloxinate |
| OW | 36.3 | Tungsten | Tungstyloxinate |
| OU | 33.8 | Uranium | Uranylloxinate |
| OZN | 19.0 | Zinc | Zinc 4-cyclohexanebutyrate |

Group II Compounds

| Cat. No. | % | Metal | Salt |
|----------|------|-----------|--------------------------------------|
| OSB | 49.7 | Antimony | Antimony Pyrogallate |
| OBE | 2.8 | Beryllium | Beryllium Benzoylacetate |
| OB | 2.9 | Boron | Dimethylphenyl Borate |
| OCR | 9.3 | Chromium | Chromium (III) 2-hydroxyacetophenone |
| OFE | 20.5 | Iron | Iron (III) 4-cyclohexanebutyrate |
| OHG | 32.4 | Mercury | Mercury (II) 4-cyclohexanebutyrate |
| OV | 12.7 | Vanadium | Vanadyl Benzoylacetate |
| OZR | 23.1 | Zirconium | Zirconyl 2-ethylhexanoate |

Group III Compounds

| Cat. No. | % | Metal | Salt |
|----------|------|-----------|-------------------------------------|
| OGA | 19.0 | Gallium | Gallium 2,4-Pentanedionate |
| OGE | 14.1 | Germanium | Diphenyl Germanium 2-ethylhexanoate |
| OIN | 27.5 | Indium | Indium 2,4-Pentanedionate |

Group I
Group II
Group III
Noble Metal and Rare Earth Organic-Solvent-Soluble Compounds

| | 5g | 25g |
|--|---------|----------|
| Group I | \$26.00 | \$104.00 |
| Group II | 35.00 | 140.00 |
| Group III | 70.00 | 280.00 |
| Noble Metal and Rare Earth Organic-Solvent-Soluble Compounds | POR | |

STA-SOL, Stabilizer/Solubilizer

This unique blend of organic solubilizing agents and metal-ion stabilizers is a universal stabilizer/solubilizer which enables preparation of stable organic atomic absorption standards in your own laboratory. The completed standards may be stored for months without precipitating or gelling.

SPEX Sta-Sol consists of a long-chain carboxylic acid to predissolve the metal compound and maintain a uniform blend in multi-element preparations; a long-chain organic amine to help stabilize Cd, Co, Ni, Ag and other ions as coordinated amine complexes; a cyclic aromatic compound to predissolve and stabilize boron, phosphorus, and silicon compounds and other metal salts; a bulky, organic diketone to stabilize Fe, Cr, V, Al, Mn, Ni and Zn ions as chelates.

A 10 ml bottle of Sta-Sol is sufficient to prepare 10 single element standards in 100 ml quantities at the 100 ppm level.

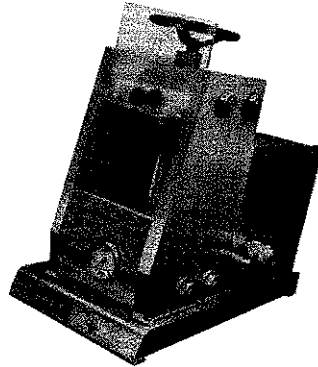
1079 STA-SOL, universal stabilizer/solubilizer with detailed application instructions

10 ml \$ 7.00
50 ml \$28.00

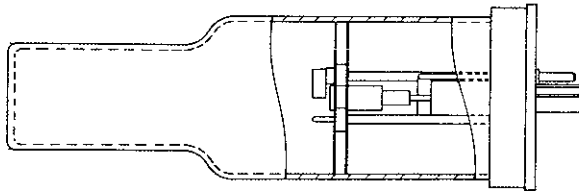
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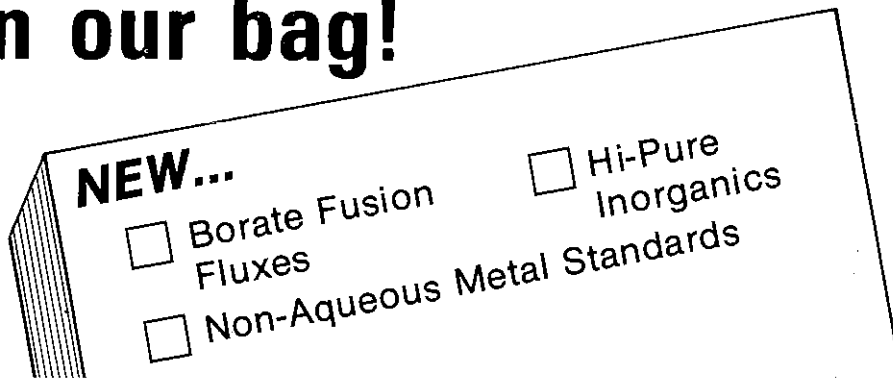


HOLLOW CATHODE LAMPS



aqueous and non-aqueous

are in our bag!



See pps. 5-11 inside for **NEW SPEX CATALOG SUPPLEMENTARY ITEMS**

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