

TRACE METALS AND MAN

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It is a fascinating hypothesis that some of the common chronic and fatal ailments of human beings may be the result of accumulations, deficiencies, or displacements of certain trace metals. Although no answers will be forthcoming here, I would like to examine this hypothesis and emphasize those metals which appear to be abnormally present in the tissues of man, those which accumulate with age against an environmental gradient, those with organ specifications and those known to be toxic. There are 29 elements around which modern thinking is based. These have been found largely through the voluminous spectrographic analyses of Tipton and her co-workers. The bulk elements (alkali metals and alkaline earths, and the non-metals) will not be discussed here leaving 20.

ELEMENTS IN THE FIRST TRANSITIONAL GROUP

In the first transitional group of elements, five—Mn, Fe, Co, Cu, Zn—are known to be essential to life and health and a sixth—Cr—will probably be elevated to that status. Deficiencies are known in cattle, laboratory animals or man. These metals are chelated to protein or to organic chemicals in the body; insofar as is known, Fe and Co largely to porphyrins, the basis of respiratory pigments in plants and animals. The metals act as metallic cofactors on various enzyme systems. Most of them are tightly bound. They all have unfilled outer shells and so act as electron acceptors and frequently as catalysts. All but Zn occur in more than one valence state. Each can displace another on certain ligands, usually in a definite order. Their relative abundance in the universe, on the earth's crust, in the ocean (whence our ancestors came) and in plants,

Since 1958 Director of Research at Brattleboro Retreat in Vermont, Henry Alfred Schroeder is an experimental medical doctor devoted to the study of the relationship between man's health and his environment. He wonders how the new materials which carry man's drinking water, which fertilize his soils, which contaminate the air he breathes, which contain his food relate to diseases. Graduating from Yale in 1919, he went on to obtain his M.D. from Columbia University in 1933. After his internship, he sidestepped into the fields of research and teaching, interrupting his civilian career during the war with service in the Navy where he attained the rank of Commander. That he is honored with membership in Sigma Xi, is the co-owner of a patent on an anti-blackout device used by the military services, has published numerous articles on his studies, is a trustee of Marlboro College, Marlboro, Vt., all testify to a career diversified, accomplished, and most of all, of immense service to his fellow man.

is quite high and they are ubiquitous. They all have a low level of toxicity by mouth to mammals and there are or appear to be mechanisms preventing excessive absorption by the gut or promoting excretion by bile or urine. When these mechanisms break down, either by hereditary absence or by imposed disorders, diseases can result in the cases of three—Cu, Fe, Mn.

Including Cr already mentioned, there are four other elements—Ti, V, Ni and Cr—which have biological activities of a catalytic nature but which are not now accepted as essential for life. Again all are relatively non-toxic, ubiquitous, reactive and non-accumulative in man.

Having just completed a large series of Ni determinations, we can report that Ni is found in all plant and plant products but not in meat, eggs or milk. We found it in gray but not in red squirrels, in two of eight wild deer kidneys and livers, in several wild birds and rabbits. Ni appears in man to a high degree of frequency only in the intestine and skin and does not accumulate with age. To add to the confusion, there is much less in people from Miami, Denver and Dallas than from Seattle and New York; there is more in Indians, Thai, Japanese, Filipinos and certain Africans than in Americans, Lebanese and other Africans. The daily intake of Americans is about 0.5 mg.

In 1956, Kikkawa, Ogita and Fugita, proposed a theory that color of pigment in nature depended upon a metal which, in turn, was transmitted by a gene. Ni is associated with whiteness in drosophila, goldfish, mice, rabbits, moths, tulips, human hair and bird plumage. Ti is associated with the color yellow; Fe with red (red hair is full of iron which is why red-heads are nicknamed "Rusty"); Mo with blue and Cu, Co and Fe with black.

Other first transitional metals have metabolic or enzymatic activities *in vivo* or *in vitro*. Ti inhibits the oxidation of cysteine, an amino acid. V causes several actions and has been shown to inhibit the formation of cholesterol in rats. Together with Sr, V causes marked stimulation of mineralization of bone and teeth in animals and prevents caries. V catalyzes various metabolic oxidations.

Cr has been shown to increase cholesterol synthesis by the liver and promote fatty acid synthesis. Ni has been shown to activate arginase, a liver enzyme. Al is suspected of being essential, having been shown to promote at least one enzymatic reaction *in vitro*.

There are two recent important findings. Wacker and Vallee showed that ribonucleic acid (RNA) from plant and animal tissue sources contained Cr, Mn and Ni in constant amounts.

Specific inheritance of the ability to accumulate one metal or another according to eye or body pigment has been demonstrated by Kikkawa. *Drosophila* mutants with white eyes absorbed Ni, while mutants with cinnabar-colored eyes absorbed Co from media containing both metals. Red goldfish absorbed Mo; white absorbed Ni from water, rejecting the other. These two findings, if applied to man, can have wide implications in genetics and point indirectly to specific functions of such metals in mammals.

Some years ago Schubert suggested that many common drugs are chelating agents and that property may explain their actions. By mobilizing, transporting or excreting trace metals, metabolic changes induced by such agents may be caused. In this connection, Scheinberg has shown that penicillamine is effective in removing excessive copper deposits in the liver and brain (characteristic of Wilson's disease).

Can a metal be transmitted as a gene? One cellular component related to genes, Ribonucleic acid, has constant amounts of Ni, Cr and Mn; both Ca and Sr have been shown to chelate with another gene nucleic acid, DNA, and be transmitted to offspring. While no Ni-deficient diseases are known and no enzymes are known to require it, the evidence seems clear that it may play at least one role. It is so prevalent that it is hard to imagine why it should not have been chosen as a biological catalyst at the early stages of life on earth.

Ti accumulates in the lungs with age. It has been shown to inhibit cysteine metabolism in liver but little more is known about it except that it has a very low order of toxicity.

V is essential for certain lower animals. Perry, in our laboratory, found that it enhanced considerably the activity of monoamine oxidase—that now popular enzyme which is supposed to have something to do with mood. A number of its aromatic substrates are oxidized by V itself. Curran's classical experiments have shown that in young men it lowers circulating levels of plasma cholesterol. It also prevents dental caries in small mammals and promotes, with strontium, a hard tooth enamel. Present informed conjectures suggest that it may have a biological role in amine, in fat and in steroid metabolism and perhaps in teeth.

Cr III has been shown quite conclusively to work along with insulin in preventing the decreased glucose tolerance of rats fed a deficient diet. There is no doubt in my mind that it plays an essential role not only in glucose but also in fat metabolism. It was the only trace metal decreasing markedly with age in man, being particularly high in new-born infants.

ELEMENTS IN SECOND AND THIRD TRANSITIONAL GROUPS

Some of the elements in the second and third transitional group metals are of interest in that they can displace the essential metals of the first transitional group. For example, there is more Nb than V in man but no one knows why. Mo VI is essential and it is found mainly in liver where it should be. W, its first cousin, can displace it and inhibit reactions catalyzed normally by Mo. Most of the other transitional elements are rare both in the body and on earth. Ag was found in almost every tissue examined spectrographically by Tipton but in concentrations far smaller than that of Cu.

Cd is probably the most interesting of this group for it is concentrated from the environment against an enormous gradient. It can displace Zn in protein and it winds up in the kidney where it forms a stable chelate. We have spent much time evaluating Cd in kidney and liver tissue from people around the world. The close association of Cd with Zn in nature, its overt toxicity, its accumulation with age, the fact that levels

are highest in Japanese and only one-ninth as much in uncivilized Africans, that animals have between 1/10 and 1/100 as much cadmium as humans, that babies have little or none—makes this metal of importance. The two major sources for man are seafood and grain. American daily intake is about 23 micrograms. In the latter, the source may be fertilizers, especially phosphates, the principal American supply of which is the Florida Bone-Valley deposit, largely made of fish teeth from Plio-Pleistocene times. Civilized man is also faced with cadmium in auto exhaust fumes and in galvanized containers. Lemonade stored in such containers can become toxic.

Another well-known toxic element is Pb which is widespread in the air, in cigarettes, in food, in soft drinks. Daily exposure is about 0.3 mg. Though closely related to Pb, Sn has a low order of toxicity but it, too, is found in the tissues of man. Pb poisoning, incidentally, is routinely treated today by injecting the patient with a chelating agent (the calcium, disodium salt of ethylenediamine tetracetate or EDTA).

I have discussed four probably essential metals—Ti, V, Cr and Ni—which do not accumulate in man. But Cd, Pb, Sn, Al do accumulate usually against an environmental gradient. If some diseases are a result of metallic imbalances we must look to these eight especially—plus Nb and perhaps Sb. Somewhere in this list may lie a clue to some disease occurring after a lifetime of exposure. The bodies of men also contain variable and inconstant amounts in 1-100 mg. quantities of As, Sb, La, Nb, Ru, Tl, Zr and larger amounts than essential of Mo and Co as well as small amounts of Be, Li and V.

As has been mentioned, Pb is chelated with EDTA but the latter is not specific. In one experiment Perry and Perry gave EDTA to eight patients for 10 days and measured the urinary excretions of eight trace metals spectrographically. Much of the body's Zn has more of an affinity to EDTA than to its normal chelate and excretion of Zn rose 10-fold, producing probable Zn deficiency in two of the patients. Mo, Ni, Ag and Sn were not removed by the EDTA but Mn almost doubled as did Pb. Much current research is centered around the use of chelating agents such as EDTA to remove excess metals but in some diseases it appears unpromising. For example, it has been calculated that it would take thousands of grams of EDDHA, itself about 40 times as effective as EDTA, to remove the excess Fe in treating nemochromatosis, a metabolic disorder in which Fe accumulates in body tissues.

NON-METALS

In modern civilized man there are at least two elements, known to be essential, which may not occur in his food supply. These are the halogens, I and F. The absence of the former, of course, has long been known to cause simple goiter or enlargement of the thyroid gland in our own Midwest where the water supply is deficient in I. Although still open to controversy, (in excess it promotes a soft enamel) the property of F in preventing dental caries is accepted by most authorities today. The first clue to the function of this element came in the early 1930s when it was noted that people in Bauxite, Arkansas, developed peculiarly deformed teeth that were, nevertheless, cavity resistant. This was eventually traced to comparatively large concentrations of fluorine in the drinking water by Petrey (after whom the stand is named) who used the CaF bandheads to determine F spectrographically. The F present in many modern toothpastes can be so determined.

Having shown that three of the halogens are nutritionally essential, researchers speculate about the fourth, Br, which like the others is ubiquitous. Unlike the others, however, not only is its concentration lower but analytical methods for its detection at trace levels are poor. Logically enough, where analyti-

cal methods have been straightforward and the thresholds of sensitivity good, findings have been more fruitful.

EMISSION SPECTROSCOPY

While defining the functions and idiosyncracies of all trace elements in the body will involve a huge research effort, one obvious first step is to find out which elements are present in different parts of the body. Several years ago, Dr. Isabel Tipton started this momentous task by obtaining and analyzing spectrographically organs from hundreds of cadavers. Tissues were obtained from autopsy specimens resulting from accidental, instantaneous death of victims in several American, Oriental and African locations. Samples of aorta, brain, heart, kidney, liver, lung, ovary, pancreas, prostate, spleen and testis were sealed in polyethylene bags, quick frozen until ready for dry ashing. For determining Ag, As, Au, Bi, B, Cd, Ga, Pb, Sb, Sn, Tl and Zn, the cathode layer method with In as internal standard was used. Four mg of tissue ash and 4 mg of graphite containing the internal standard were mixed and placed in the crater of an 1/8" dia. electrode which was made the cathode in a 10 amp. dc arc. The cathode layer was focused on the slit of a large Littrow spectrograph and the region 2400-3400Å was photographed on SA No. 2 plates together with suitable standards. For the elements Al, Au, Be, Ba, Ca, Cs, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, Nb, Ni, P, Sr, Ti, V and Zr a second burning was made with Pd as internal standard. Five mg of tissue ash were mixed with 10 mg of graphite containing the internal standard and the mixture placed in the crater of a 3/16" dia. electrode. The electrode was made the anode in a 5 amp. dc arc, the spectrum again photographed on a SA No. 2 plate.

Although Tipton's results are reported semi-quantitatively, all samples were run in duplicate against two synthetic sets of standards, one representing soft tissue, the other bone. For the analysis of the latter, the method had to be modified because bone ash is about 20 times that of soft tissue, reducing the sensitivity by an equivalent amount. One modification of the method was to use a faster plate (103-F) in place of SA No. 2.

In her results, Tipton pointed out two elements which varied with the age of the individual. Cr, in kidney, liver and lung tissue, starts high in a new-born infant but drops sharply with age—a unique behavior, especially in view of the fact that Cr is probably one of the required elements. Is it possible that another confusing variable is entering the picture, an element essential in the nutrition of a rapidly-growing child but unessential to the adult? Or are there several roles for Cr, at least one of them performing only in early life?

As contrasted with Cr, Sn builds up with age of the individual, occurring in the kidneys of only 12% of the infant specimens but building up to almost 100% in early childhood. This kind of variation is typical of a non-essential element which is absorbed by the body in its environment. As mentioned earlier, elements such as Sn and Cd (which build up to an ultimate very high value in the kidney) are particularly worthy of study because of the possibility that they may unbalance the metabolism.

Strengthening the argument about trace-element imbalance is a clue reported by Kobayaski who made a geographic study of the death rate from apoplexy in Japan where the overall rate is about six times that of the U.S.A., England or Germany. Within Japan itself he found that the apoplexy rate varied considerably and could, in turn, be correlated with the SO_4/HCO_3 ratio of the river water. A land of volcanos, Japan's rivers constantly leach out volcanic ash and are frequently heavily acid and mineral laden as a result. In the region where

minerals are concentrated most, the apoplexy rate is highest. Following his clue, Kobayaski went on with his spectrographic analyses to show that, near those Italian rivers which leach volcanic ash, the death-rate from apoplexy, while not as high as the Japanese, is considerably higher than the American. We, too, found an association with drinking water and cardiovascular death rates in the U.S., which has recently been demonstrated in England and Wales by Morris *et al.*

Butt, *et al.* studied the trace element balance in several disease states using a direct reading spectrometer. Like Tipton's technique, the authors' consisted basically of a dc arcing of the ashed tissue, controls being obtained from routine autopsies. After obtaining these control concentrations in a group of organs, the results were compared with the analyses from organs of diseased individuals. One conclusion was a verification of the work of Vallee, that the Zn content of the livers of individuals who died from Laennec's cirrhosis is lower than that of normal individuals. Vallee also showed that Zn in urine of cirrhosis patients was higher than average, suggesting that their ability to utilize the metal was impaired. By showing that Zn was lower in organs other than the liver, Butt went one step further to prove this theory.

Butt also studied organs of individuals who had died from three diseases involving iron build-up. Bantu siderosis, hemochromatosis and sickle cell anemia. In siderosis, where enormous quantities of Fe are found in the liver, Pb, Mo and Ca were found to be 6-8 times higher than normal. Cu and Zn, on the other hand, hovered around the normal. The pattern for hemochromatosis, with almost as high an Fe content in the liver as Bantu siderosis, showed a lower Mo build-up than the latter and the Al content was only about one-tenth the control median.

It must be emphasized that the studies of both Tipton and Butt provide only preliminary information subject to some correction as the variables, one by one, are ironed out. Butt noted considerable variation in the normal trace-element values of people in Los Angeles and New York City. The interesting decrease with age of Cr, the extraordinary build-up in civilized man of Cd in the kidney, the fact that organs should be fractionated as much as blood is before analysis, greater analytical accuracy—these are all considerations which must be studied before conclusive results can be achieved.

Feldman of Oak Ridge National Laboratory is working along the line of analytical accuracy, attempting to use the best possible spectrographic methods on a very large number of samples. In a sense, he is setting up a mass-production spectrographic laboratory where the entire procedure, from obtaining samples to recording results, will be done as swiftly and accurately as possible. Instead of relying on dozens or even hundreds of results, Feldman is hoping to obtain thousands, eventually to tabulate and analyze the information on a computer.

One of the surprising elements found essential by the emission spectrograph was Co. A wasting disease among Australian sheep called pining baffled researchers for many years until it was noted that the soils on which suffering animals grazed contained no cobalt. The soils in Australia are sandy, easily leached by water and, in this respect, resemble those in parts of Scotland where Mitchell soon confirmed a Co deficiency among sheep. Grazing animals, obtaining their lifetime food from a compact area, are most susceptible to nutritional deficiencies and, although this was suspected, it was not until around 1940 that Co was considered. Not essential to plants, this element was particularly difficult to track down because the plants in affected areas remained healthy although they did not carry the Co to the animal.

Co is, of course, now known to be part of the molecule of vitamin B-12, a few micrograms of which are required daily. Many of the other essential elements are parts of the molecules of enzymes. Metalloenzymes are being discovered at an increasing rate and appreciation of their importance in human nutrition is widening. Many enzymes depend upon Mn, especially several peptidases which help digest proteins. At least one enzyme is Co dependent. The Cu oxidases which catalyze the reduction of molecular oxygen are well known. Six Zn metalloproteins have been isolated, five by Vallee and his co-workers. There are two mammalian Mo enzymes.

METAL DEFICIENCIES AND DISPLACEMENTS

As already pointed out, soils and plants deficient in one or more trace elements are well known. Deficiencies can be transmitted to livestock grazing on grasses and, thereby, presumably to man. Many soils of the world are deficient in Mo, Cu, B, Co, Mn or Zn.

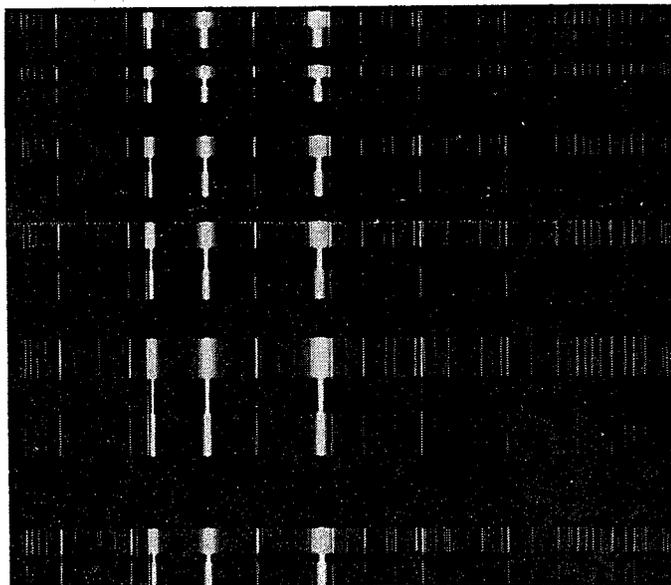
Mn deficiency has been suspected in a certain skin disease. Cu deficiency has not been demonstrated in adults but, in children it has been suspected in types of anemia. Postalcoholic cirrhosis of the liver has been found to be associated with

plasma and liver Zn deficiency by Vallee with some reversal when Zn salts were fed.

It is not necessary for there to be an absence of a particular essential element for the body to show a deficiency in it. Similar ions will compete one for the other. Thus, while Ag and Au appear unessential, there is some evidence that they will compete in reactions where Cu is required. Furthermore, Cr will compete with two lower valences of Mo. There are examples in biological systems where, by displacing Mg on a Mg dependent enzyme, Be inactivates it. All group II alkaline earths tend to concentrate in bone.

Although it is impossible to apply these considerations to clinical states at this time, the presence in a tissue of high concentrations of an unessential element with characteristics similar to that of an essential element makes the former suspect. Such imbalances are possibly contributory in many diseases such as atherosclerosis, cancer, allergies and hypertension.

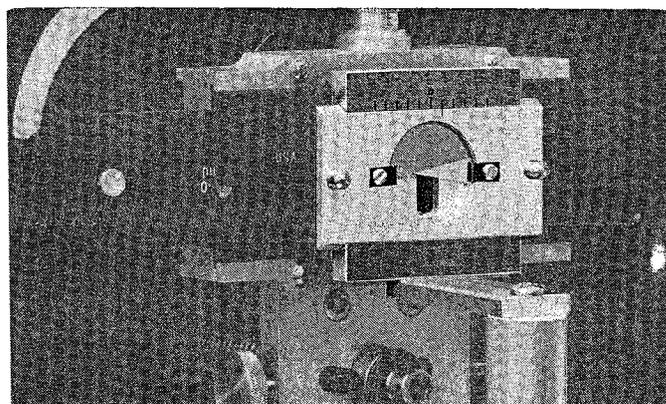
With the increasing awareness of the roles of trace elements in metabolism has come a need for better—more accurate, sensitive and simpler—methods of analysis. Although chemical analyses are sometimes more sensitive for a particular element, the emission spectrograph offers one of the best multi-element tools for the purpose.



Spectra taken with the No. 1090 Three-Step Filter. The top spectrum is a two-step (100% and 20% T.) masked down to about 1.5mm per step. The next four spectra show how, by sliding the filter and the fishtail, the middle (4% T.) step and the other two may be varied in height. The fifth spectrum illustrates a three-step spectrum set to the maximum heights of about 5mm for each step.

THREE-STEP NEUTRAL FILTER

When a number of elements are to be determined simultaneously, the spectrographer is usually faced with the annoyance of finding lines of certain elements over-exposed while those of others are under-exposed. One solution is to use a stepped sector or filter which attenuates the light neutrally. The former has the disadvantage that two adjacent steps differ in attenuation by a factor of only 1.5 to 2. In practice a factor of 4, permitting that much more latitude in exposure, is more desirable. A typical example of a problem well known in most laboratories where such attenuation would be useful is the over-



No. 1090 Three-Step Filter mounted close to the slit of a stigmatic spectrograph. The fishtail on the slit is used to adjust the heights of the two outer steps.

exposure of the copper and silver lines, no matter how low the concentration of these elements, in the 3250A region.

The No. 1090 three-step neutral filter reduces the density of such lines to readable values. As shown in the accompanying sketch, the three steps of 100%, 20%, and 4% transmittance are arranged on a fused quartz, optically flat and polished disc one inch in diameter. The filter is constructed with wedges of evaporated metal and is so mounted in a slide that it can be pushed horizontally across the center of the optical path. Thus, when placed at the focus position (the slit in stigmatic spectrographs, Sirk's focus in astigmatic instruments), the height of the steps can be made to vary up to about 5mm, when used in conjunction with the fishtail of the spectrograph. Furthermore, it is possible to utilize either the 20% filter alone or the 5% and 100% as a two-step filter simply by sliding it in place. An engraved scale is provided to permit resetting positions.

The No. 1090 filter is mounted on an offset post to fit standard riders and still be placed as close as possible to the position of vertical focus.

1090 Three-Step Neutral Filter Assembly, on offset post. Please specify the diameter of the post necessary to fit the rider of your spectrograph (normally 1/2", 5/8" or 3/4")\$145.00

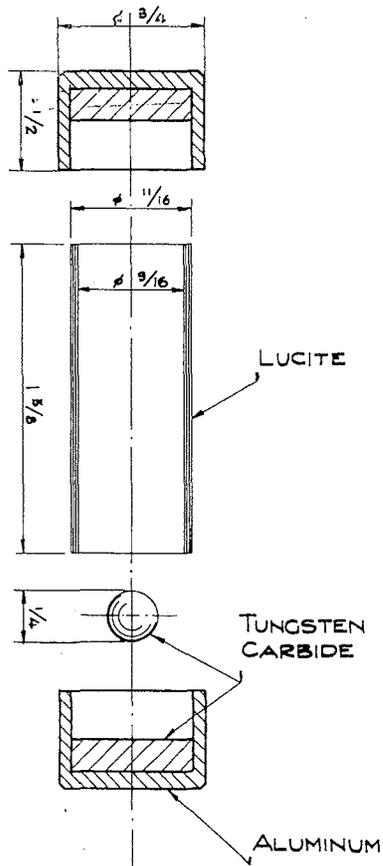
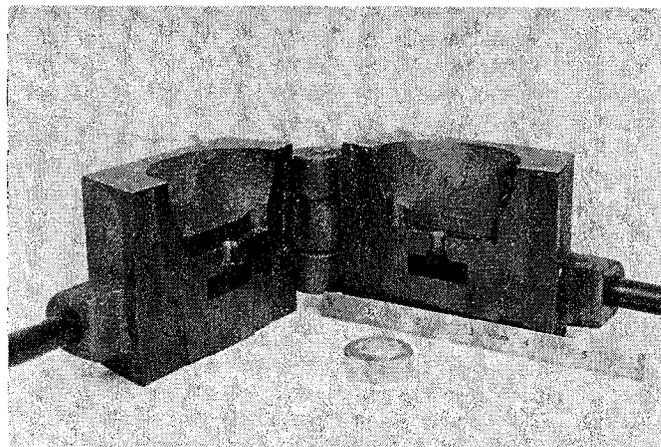
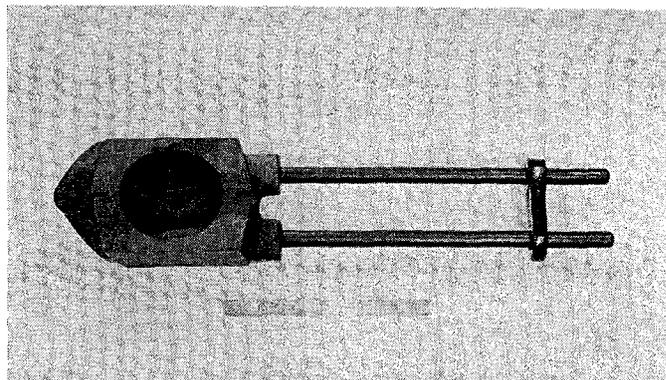
1-1/4" DISC BOOK MOLD

A couple of years ago both the National Bureau of Standards here in this country and the Bureau of Analysed Samples in England decided to standardize on a 1-1/4" diameter disc size, the idea being that one size would serve both the emission and x-ray fields. While this has not been fully accomplished as yet, NBS will, where possible, upset forge its older sizes to this diameter and most future standards will probably be so prepared.

We are now supplying a cast iron book mold to prepare discs of low-melting alloys just under 1-1/4" in diameter by about 3/8" thick. This will permit spectrographers to match their samples to the standards and so facilitate set-ups, minimize machining, and further boost accuracy.

In operation, the two halves of the book mold are closed and latched. Molten metal is poured into a wide funneling cup. The large mass of the mold quickly freezes the casting and the sample is removed almost immediately. The disc is cast horizontally to promote immediate chilling at the bottom surface. This usually results in small, uniform grain structure along the surface of the sample to be analyzed. A minimum of machining or sanding is required because the faces of the mold are machined quite smoothly.

3904 Book Mold, for casting discs about 1-1/4" dia.
x 3/8" thick **\$70.00**



SMALL TUNGSTEN CARBIDE VIAL

Our No. 8004 tungsten carbide (Kennametal) vial is widely used in conjunction with the No. 8000 Mixer/Mill. Having a capacity of 60 ml and a grinding capacity of about 1/3 that, a comparatively large size sample can be pulverized in short order.

Until now, however, because of weight limitations, it was not possible to use this extremely hard, high-impact material in a vial for the smaller No. 5000 Mixer/Mill. This problem has been solved by utilizing a Lucite center section cylinder with tungsten carbide lined end caps, as shown in the accompanying drawing. The vial has a volume of 8 ml and a grinding capacity of 2-3 ml.

For laboratories handling large numbers of small samples, four of the No. 5004 WC vials may be placed simultaneously in the No. 8000 Mixer/Mill using the special adapter No. 8014.

5004 Tungsten carbide grinding vial , consisting of two tungsten carbide lined end caps, six replaceable center sections of Lucite, two 1/4" dia. tungsten carbide balls	\$30.00
5004A Tungsten Carbide Ball , 1/4" dia., spare	(4) 2.00
5004C Lucite Center Sections , spare	(6) 10.00
5004W Tungsten Carbide Lined End Caps , spare	(2) 20.00
5000 Mixer/Mill , 115v 60 cy, or 230v 50 cy (specify)	140.00
8000 Mixer/Mill , specify either:	115v 60cy 330.00
.....	230v 50cy 338.00
8014 Vial Adapter , for holding four No. 5004 tungsten carbide grinding vials in No. 8000 Mixer/Mill	14.00

READERS' COMMENTS CONCERNING

"WORK AHEAD IN EMISSION SPECTROSCOPY"

which appeared in

SPEX SPEAKER — Vol. VI, No. 1

A number of readers have been kind enough to comment on my article, "Work Ahead in Emission Spectroscopy." Not surprisingly, errors especially of omission, were found. H. F. Nicolaysen, Continental Oil Company, Ponca City, Oklahoma, pointed out that the use of cyanogen bands for the determination of nitrogen in organic compounds was reported by Fredrickson and Smith (*Anal. Chem.*, 23, 742, 1951). V. A. Fassel, Iowa State University, Ames, Iowa, noted that, contrary to what was stated, there is a good deal of basic research being done and reported. He mentioned the work of European spectrographers particularly and their reports in *Colloquia Spectroscopica Internationales*. The 1959 proceedings of this colloquium have just been published by and are available from H. R. Sauerlander & Co., Aarau, Switzerland.

C. H. Corliss, of N.B.S., sent a reprint (*Spec. Acta*, 5, 378, 1953) of his article on the effects of circuit parameters on the excitation of spectra—a subject that the article indicated was not well explored. In his paper, Mr. Corliss presented an excellent mathematical treatment of capacitor discharges, correlating theory with the intensity of arc and spark lines. In my opinion, however, the article leaves much ground uncharted. What are the effects on line/background ratio of changes in source parameters? is an open question still awaiting a comprehensive study by some aspiring PhD. candidate.

Miss V. M. Vought, of the State Occupational Health Laboratory, Harrisburg, Penna., noting my reference to the lack of data on laboratory temperature and humidity effects, wrote that she was prompted to keep records of humidity and temperature, suspecting that these were responsible for shifts in the analytical curves obtained for beryllium in air. Thus far, she indicated, attempts to correlate these data have not been too successful. Far from being discouraged, however, she is now planning to set up a barometric pressure recorder as well. I feel that, eventually, she will be rewarded with an answer, partial or complete, showing that the ambient atmosphere in the laboratory does, indeed, affect analytical curves.

Sympathetic to my call for more research in spectroscopy, W. F. Meggers, of the N.B.S., pointed up the sparsity of measurements of the exact wavelengths of spectral lines. Considering the advances in instrumentation and theory since most measurements were made, almost every line should be both remeasured and reassigned, if necessary.

The most extensive criticisms of the article came from A. H. Gillieson, Department of Mines and Technical Surveys, Ottawa. From his letter, the following is quoted:

"Regarding the use of metallic electrodes, suggested in Par. 8, I recall a very flexible and useful method, developed by my colleagues (Nickelson, Stubbs and Garton) in my old department, the U.K. Ministry of Supply Chemical Inspection Dept. In my opinion this Iron Flux Method was published

somewhat obscurely and deserves wider attention. The sample was mixed with pure ferrous ammonium sulphate or pure ferrous sulphate and ammonium sulphate, made into a small pill and placed on the lower of two 1/4 in. to 5/16 in. pure copper electrodes. Initially arcing took place between the electrodes, but after a few seconds, transferred to the pill, when the shutter was opened and exposure continued until the sample neared exhaustion and the copper spectrum recognisably reappeared. Currents were low—certainly not much above 7 amps. The only reference I can lay my hands on, is the British A.E.R.E. Report AM-46 obtainable in the U.S.A., I believe, through the U.S.A.E.C.

"Paragraphs 11-12 raise two very interesting points. I have used both the copper and the graphite spark for U and Pu and confirm the great sensitivity achieved. The source used was a specially built 30KV high-voltage Feussner source unit. (Capacitance 0-0.02 μ f; Inductance 0-220 μ h) and with this, sensitivities from 0.25 x 10⁻⁸g. for Be to 8 x 10⁻⁶g. for Rb and Cs were recorded, using a 100 μ g sample.

"Your comment on the hollow cathode as a shelf curiosity in para. 13 interested me, since I pioneered its use in the U.K. and I am a firm believer in its potentialities. It was employed successfully for the determination of fluorine in very small quantities (46 μ g) of organic compounds, and sensitivities of 0.1-5 μ g for the halogens and for the alkali metals were obtained. Practically alone amongst source units, has one the degree of control of current and voltage and temperature possible in the hollow cathode.

"In para. 14 you quote Van Cittert's criterion (Sawyer p. 111), which is not quite correct, as was pointed out in 1948 by Professor Croze of the Sorbonne in a paper presented to G.A.M.S. and published in their Proceedings.

Under the heading 'Determination of Non-Metals', paras. 1, 3-5 were most stimulating. As I pointed out above, the hollow cathode is a very suitable source both for non-metals, particularly halogens, and also for the examination of organic compounds.

"Under instrumentation did you notice the use of the Allen photomultiplier (obtainable from Bendix Instruments) as a detector for the 'hole' from soft X-rays to 1650A? Refs. *Rev. Sci. Inst.* 23, 8, (1952) and 31, 280 (1960); 100-800A. W. L. Garton of the Physics Dept., Imperial College of Science, London, England has been using these photomultipliers for the region 500-1800A (I believe) since about 1952.

"I don't intend these comments in any critical sense but merely to show the reaction of one spectrographer to your stimulus and challenge."

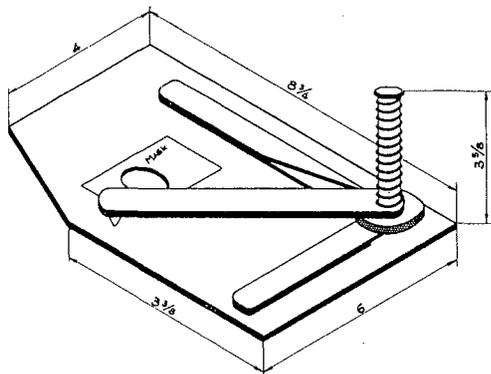
—A. J. M.

HIGH-PURITY GRAPHITE VIAL

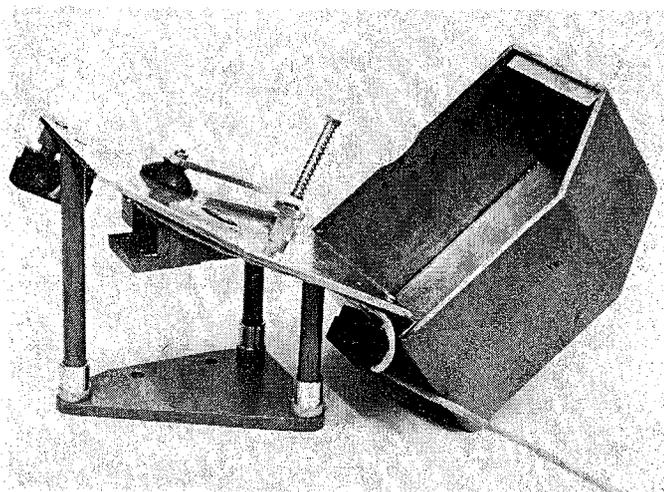
When organic samples are analyzed spectrographically, the usual procedure is to ash them first in platinum or Vycor, transfer the contents to a plastic vial and mix with an appropriate weight of lithium carbonate or other buffer. Not only does the procedure involve a transfer operation which can be difficult because of adherence of the ash to the walls of the container but metallic contamination from the latter is always a possibility. In many instances the procedure can be simplified as well as "contamination-proofed" through the use of our high-purity, No. 3120, graphite vials. The sample is ashed directly in the vials at a maximum temperature of 500°C and the buffer added to the same container. Using a Lucite ball and a polyethylene cap (ones supplied with our No. 3111 and No. 3116 polystyrene vials fit), the contents are ground in the Wig-L-Bug or No. 5000 Mixer/Mill.

It should be cautioned that not all materials can be ashed in graphite because of its comparatively low oxidizing temperature. If the temperature is raised above 500°C, the graphite not only will decompose but, in doing so, prevent the oxidation of the contents. On the other hand, it is usually a good plan to ash at as low a temperature as possible (under 450° is generally recommended) in order to avoid loss of such volatile elements as arsenic, zinc, mercury, etc.

3120 Vial, high-purity graphite, 1/2" dia. x 1" long, for ashing up to 500°C and subsequent grinding and blending of samples without transfer....(48) **\$24.00**



The surface dimensions of the No. 3522 Bulk Specimen Stand.



BULK SAMPLE STAND FOR X-RAY ANALYSIS

General Electric XRD-3 and XRD-5 spectrometers are equipped with a small sample drawer for holding specimens up to about 2" in diameter by 1/2" thick. Larger samples must be cut prior to analysis. At best this is another operation adding to the cost of the analysis but often it is uneconomic to ruin a sample by cutting it up. The No. 3522 Spex Bulk Sample Stand permits the analysis of most samples directly. Although the limiting size is determined somewhat by its shape, a piece up to about 4" x 8-1/2" x 3-7/8" can be analyzed, and by removing the protective interlocking cover, larger samples still can be accommodated.

To use this Stand, it is first necessary to invert the optics of the spectrometer through the use of our Inverted Optics Kit No. 3521. The x-ray tube is turned through 180° so the beam, normally pointed down, is directed upwards requiring the optics, detector and sample holder to be remounted on stands about 4" above their usual position.

For safety, two micro switches are wired in series with the start switch of the spectrometer and must be depressed simultaneously before the x-ray beam can be energized. Located at diagonally opposite corners of the base plate, the switches are ordinarily actuated by the hinged cover which serves as a radiation shield as well. If, however, the sample to be analyzed is too large, the cover is removed altogether and the weight of the sample can actuate the microswitches. When this is done, it is, of course, necessary to take precautions against scattered radiation.

The base plate of the No. 3522 Stand is undercut to fit the aluminum masks, provided with standard sample holders, and once set up, it should not be necessary to return the instrument to its old optics because small as well as large samples can be analyzed with equal convenience. In fact, with a special mask (No. 3522-L) liquids, too, can readily be analyzed using our No. 3515 polypropylene, expendable liquid cells.

Because the surface of the Bulk Stand is inclined about 30°, means are provided to keep samples from sliding off the base. A hold-down arm is spring-loaded against the top of small samples; large samples are kept from sliding by two swiveling arms which may be locked into the required position.

- 3522 Bulk Sample Stand**, for analyzing large samples on General Electric XRD-3 or XRD-5 spectrometers. Mounts on table of instrument; standard G.E. collimator screws to one end; two safety switches are wired through cable (provided) in series with start switch. (Requires Spex No. 3521 Inverted Optics Kit) **\$300.00**
- 3522L Mask**, aluminum for No. 3515 Liquid Cells. This mask may also be used in the regular sample holder provided with XRD-3 or XRD-5 spectrometers **9.00**
- 3521 Kit for inverting optics** on G.E. spectrometers XRD-3 or XRD-5 **245.00**
- 3515 X-ray Liquid Cells**, expendable polypropylene
 100 **8.00**
 1000 **53.00**
- 3516 Teflon Rings** for No. 3515 cells
 6 **5.00**
 100 **70.00**
- 3517—Mylar**, 1/4-mil Film, 2-1/2" x 100 ft.(roll) **3.50**

AN OPEN LETTER

We have been informed by United Carbon Products Company, Inc. that, effective June 1, 1961, all of its dealerships will be eliminated. What prompted the management to do this is not clear but, evidently, they hope to profit by it.

Naturally, we want to continue to serve your electrode needs and to do this will still offer National Carbon electrodes. As you know, graphite and carbon materials provided by both firms are almost identical so there should be no problems whatsoever in substituting one for the other. In order to assure you, however, that no differences do exist for your applications, we would like to offer you sample electrodes of any types you would like to try. Please tell us which ones to send.

This is an opportune time to tell you that, in our opinion, National is doing a beautiful job in constantly improving its products. Recently, you will remember, they designed a new type of package to minimize breakage in shipment and to facilitate the removal of electrodes. Plastic boxes instead of glass are used to prevent the possibility of silicon contamination. Last month, at the Chicago SAS meeting, another—and more significant—improvement was made. Hereafter, the purity of electrodes will be designated by actual figures rather than the nebulous O, X, 1, 2, etc. relative values reported earlier. A typical analytical slip will read as follows:

Al.	0.1 ppm
Mg	1.2 ppm
Fe	0.4 ppm
Si	1.8 ppm

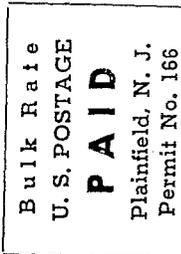
Unlisted elements are not detected. The total impurity content of all elements is guaranteed to be less than 6 ppm.

Too infrequently do we have an occasion, such as this, to thank you for the privilege of supplying not only your electrode requirements but also other spectrographic products we manufacture and distribute. It is through your patronage that Spex has been able to make available the increasing number of standards and accessories which improve the efficiency of our laboratory day.

SPEX

INDUSTRIES INC.

P. O. Box 98
Scotch Plains, N. J.



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