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Research and Development

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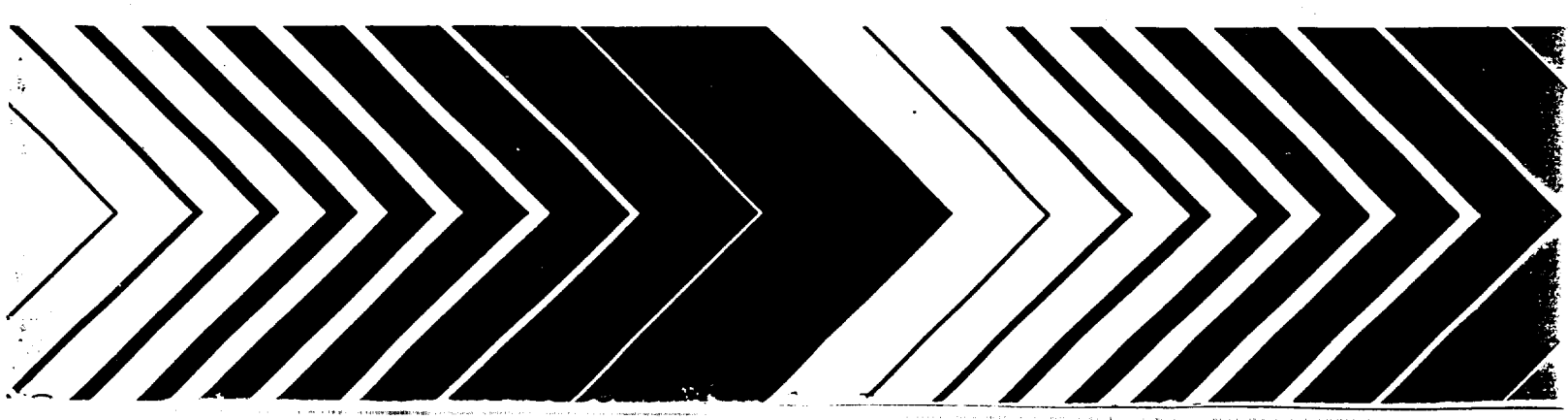
Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples



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ANALYSIS OF PESTICIDE RESIDUES IN HUMAN AND ENVIRONMENTAL SAMPLES

A COMPILATION OF METHODS SELECTED FOR USE IN PESTICIDE MONITORING PROGRAMS

REVISIONS BY

THE ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS

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MISCELLANEOUS INFORMATION

CLEANING OF LABORATORY GLASSWARE

In the pesticide laboratory involved in the analysis of samples containing residues in the parts per billion range, the preparation of scrupulously clean glassware is mandatory. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from contamination. Particular care must be taken with glassware such as Kuderna-Danish flasks, evaporative concentrator tubes, or any other glassware coming in contact with an extract that will be evaporated to a lesser volume. The process of concentrating the pesticide in this operation may similarly concentrate the contamination substance, resulting in extraneous chromatographic peaks that, in extreme cases, may completely overlap and mask the pesticide peak pattern.

Although chemists do not all agree on procedural details in the cleaning of glassware, the majority are in agreement regarding the basic cleaning steps. These are:

1. Removal of surface residuals immediately after use.
2. Hot soak to loosen and flotate most of soil.
3. Hot water rinse to flush away flotated soil.
4. Soak with deep penetrant or oxidizing agent to destroy traces of organic soil.
5. Hot water rinse to flush away materials loosened by deep penetrant soak.
6. Distilled water rinse to remove metallic deposits from the tap water.
7. Acetone rinse to flush off any final traces of organic material.
8. A preliminary flush of the glassware just before using with the same solvent to be used in the analysis.

Each of these eight fundamental steps will be discussed in the order in which they appear above.

1. As soon as possible after use of glassware coming in contact with known pesticides, i.e., beakers, pipets, flasks or bottles used for standards, the glassware should be acetone flushed before placing in the hot detergent soak. If this is not done, the soak bath may

4. The most common and highly effective oxidizing agent for removal of traces of organic soils is the traditional chromic acid solution made up of H_2SO_4 and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40° to 50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves and apron. The bench area where this operation is conducted should be covered with lead sheeting as spattering will disintegrate the unprotected bench surface.

   The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca 0.1 N NaOH upon dilution and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attach glass nor exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex" a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware may pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended as contaminants may be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware then can be inverted and suspended to dry. Small articles like stirring rods, glass stoppers and bottle caps can be wrapped in aluminum foil and oven dried a short time if oven space is available. Under no circumstance should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

stop

serve to contaminate all other glassware placed therein. Many instances of widespread laboratory contamination with a given pesticide are traceable to the glassware washing sink.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard water scum or curd would have an affinity particularly for the chlorinated pesticides and, being almost wholly water insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form is manufactured by Alconox, Inc., New York and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

   NOTE: Certain detergents, even in trace quantities, may contain organics that will contribute significant background contamination by electron capture detection. For this reason any detergent selected should be carefully checked to ensure freedom from such contamination. The following procedure is recommended:

   Add 25 ml dist. water, previously checked for background contaminants, to a 250 ml sep funnel. Add 1 drop of the liquid detergent (50 mg if in powder form), followed by 100 ml hexane. Stopper funnel and shake vigorously for 2 minutes. Allow layer separation, draw off and discard aqueous layer. Add a pinch of anhydrous Na_2SO_4 to the hexane extract and shake 1 minute. Transfer extract to a Kuderna-Danish assembly fitted with a 10 ml evaporative concentrator tube containing one 3 mm glass bead. Reduce extract volume to ca 3 ml in a hot water bath. Cool, rinse down ⅋ joint and sides of tube with hexane, diluting extract to exactly 5 ml. Stopper tube and shake on Vortex mixer 1 minute. Chromatograph by electron capture GLC and evaluate chromatogram for contaminant peaks.

3. No comments required.

Pipet Washing

The efficient washing of pipets offers some special problems. Hand washing performed by soaking pipets in a pan or sink followed by rinsing under running water is highly unsatisfactory, particulary as applied to transfer or volumetric pipets. This procedure does not assure a complete rinse of all surfaces inside the bulb. Therefore, an automatic or semi-automatic washing system is strongly recommended. Self-contained equipment for the entire operation, although available commercially, is quite expensive.

The basic cleaning steps are the same as those listed earlier for miscellaneous glassware, with the exception of the soap wash.

After use, all pipets should be rinsed with an appropriate solvent to remove the bulk of residues remaining in the pipets. The pipets are cleaned by immersion in a chromic acid cleaning solution. For this purpose, the pipets should be in a standard (13.5 x 44 cm) nalgene pipet basket. The entire assembly is submerged in chromic acid in a glass cylinder (16 x 39 cm). After 1-2 hours, the basket of pipets is withdrawn from the chromic acid solution, allowed to drain about 1 minute, and then transferred to a stainless steel washer where rinse water (tap) is run through the washer at the rate of ca.3 minutes per discharge for approximately 1 hour. If piped distilled water is available, seven or eight discharges of this are run through the system to remove all traces of metal contaminants left by the tap water.

A final rinse with acetone, either from a wash bottle or from an overhead syphon bottle, is then applied to each pipet. After draining, a convenient and rapid method of drying is to wrap a bundle of pipets in aluminum foil and place in a drying oven for at least 3 hours, or overnight.

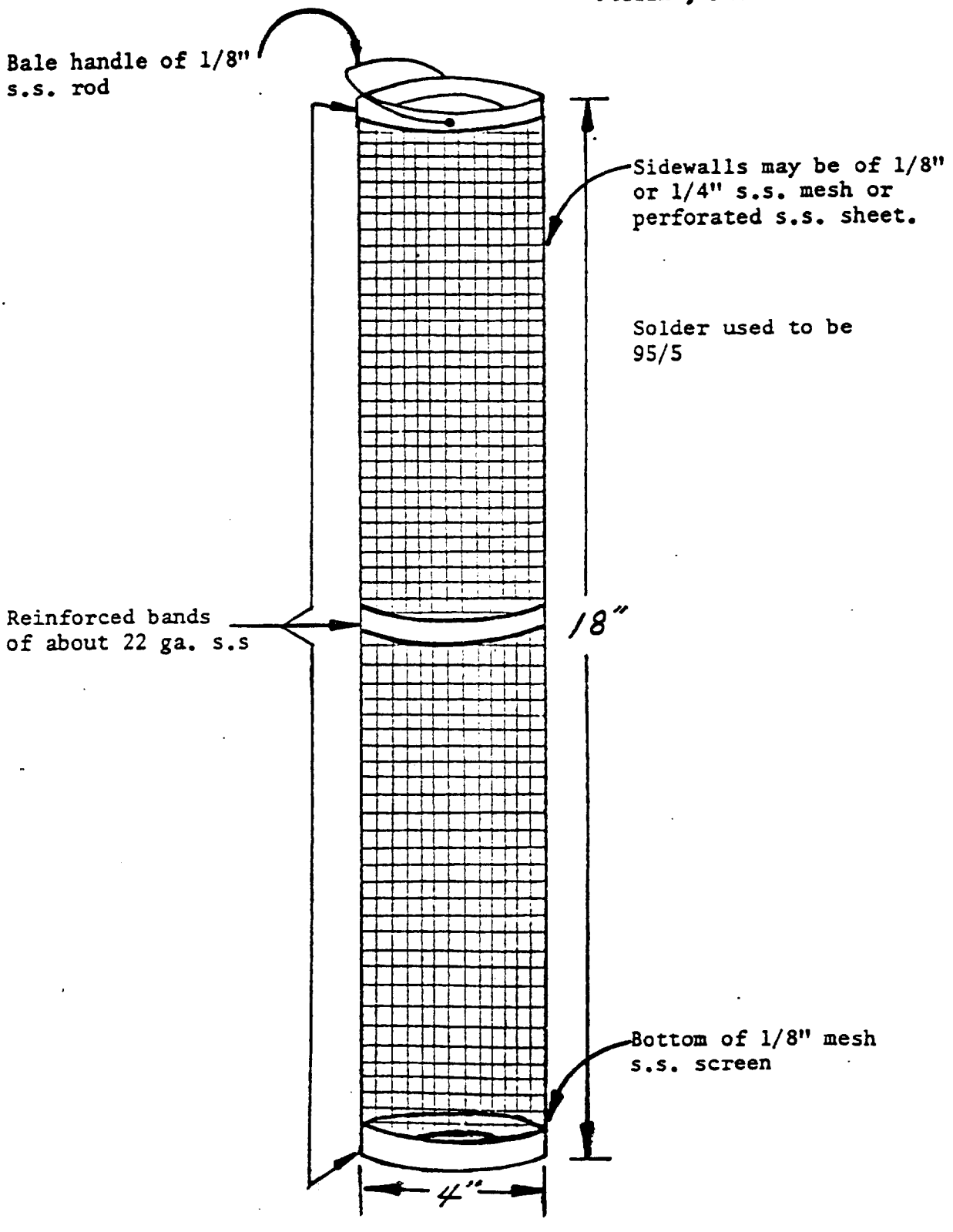
NOTES: (a) Under no circumstances should plastic gloves be worn by personnel during glassware cleaning or handling. It has been determined beyond question that these gloves can most effectively contaminate an entire sinkful of glassware to such an extent that subsequent solvent rinsing may not completely eliminate the contaminants. This is a VERY IMPORTANT precaution.

(b) Drying racks of plastic or plastic-coated metal must be avoided. The latter type of rack may be used, however, after the plastic is scraped from the metal prongs and the rack is cleaned thoroughly with a suitable organic solvent.

FIGURE 1.

PIPET BASKET

Perrine Primate Research Branch
P.O. Box 490
Perrine, Florida 33157



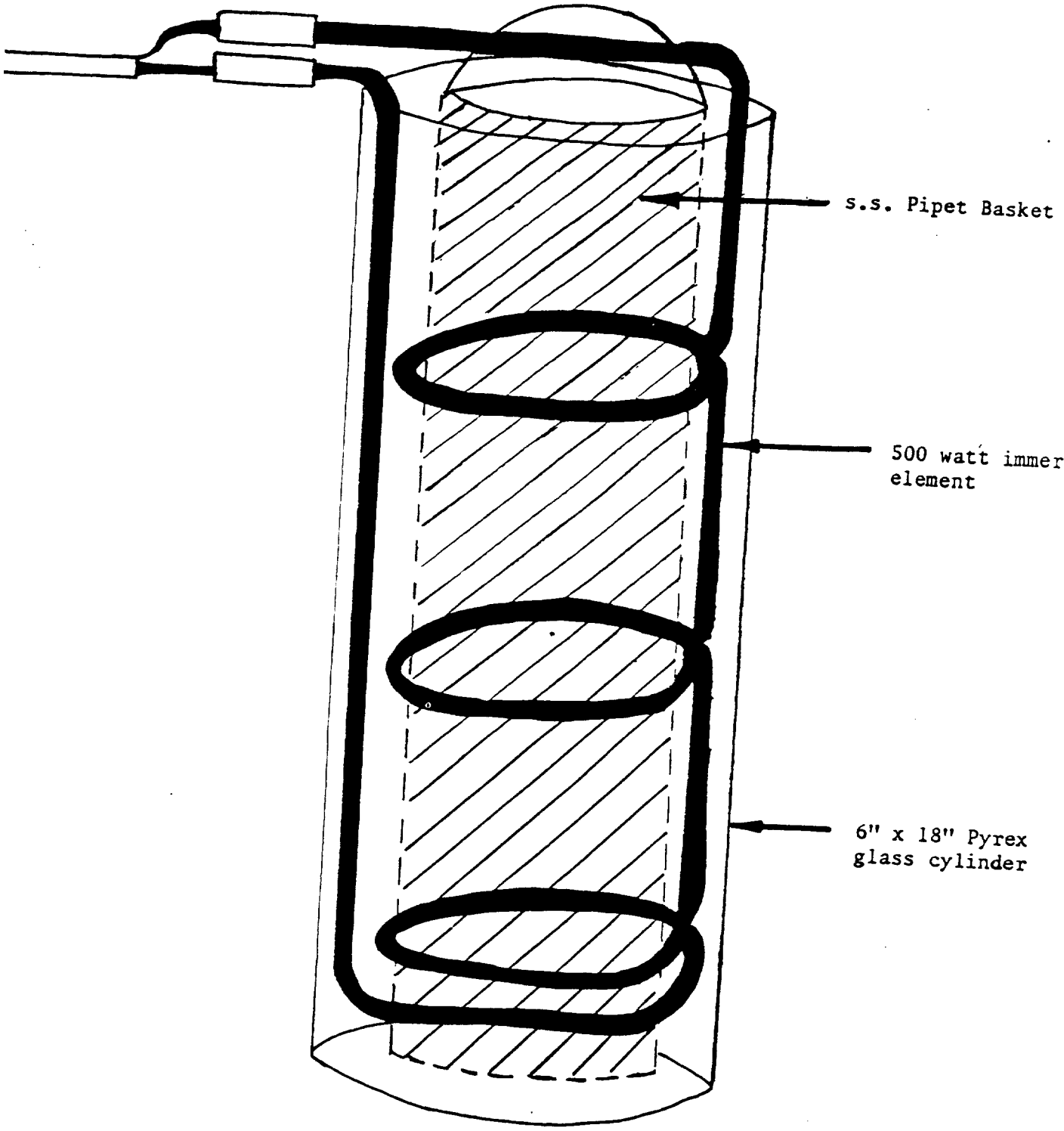


Figure 2. Assembly of pipet washer showing pipet basket inside coiled immersion heater, all contained in Pyrex jar.