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MICRODROPLET SAMPLE APPLICATION IN ELECTROTHERMAL ATOMIZATION F--ETC(U)

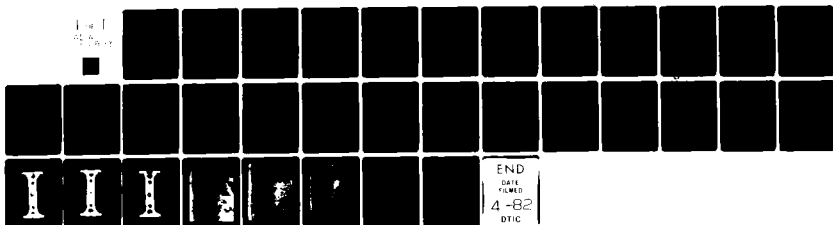
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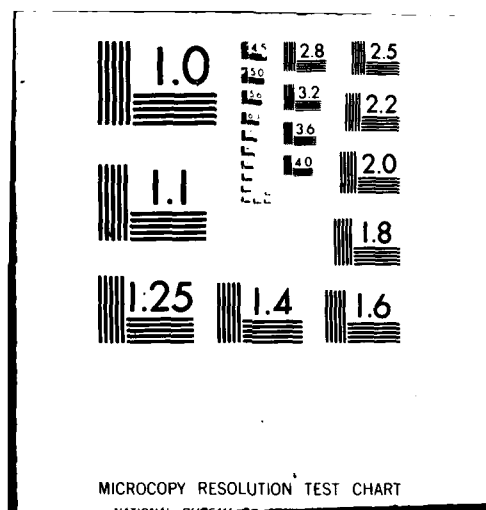
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TECHNICAL REPORT NO. 44

MICRODROPLET SAMPLE APPLICATION IN ELECTROTHERMAL
ATOMIZATION FOR ATOMIC ABSORPTION SPECTROMETRY

by

J. G. Shabushnig and G. M. Hieftje

Prepared for Publication

in

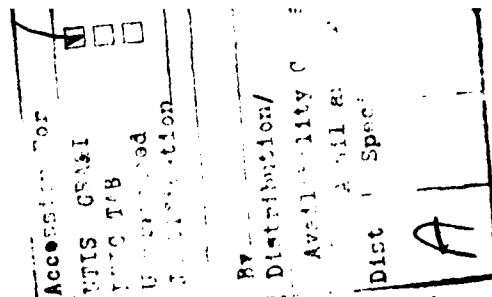
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The application of liquid samples in the form of microdroplets, approximately 150 microns in diameter, to an electrothermal atomizer has been evaluated. This technique has been found to offer improved precision (1-2% RSD), microsampling capabilities, and simplified calibration using a single concentration standard. Examination of dried sample after deposition indicates reduced spreading and crystal size for microdroplet and aerosol deposition compared with manual micropipetting methods. Crystal size and deposit spreading were found to correlate with the degree of suppression of Pb signals by Cl^- and of Au signals by sulfate.

Electrothermal atomization (ETA) in atomic absorption spectrometry (AAS) has remained a valuable tool for elemental analysis, despite the recent introduction of the inductively coupled plasma. This value is due primarily to efficient sample use and the superior sensitivity achieved with ETA, typically 2-3 orders of magnitude better than that obtained by flame atomic absorption or plasma emission spectrometry [1].

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Attempts to overcome these difficulties have included the construction of accurate positioning devices for syringe-based dispensers [6-8] and the deposition of sample as an aerosol onto a preheated atomizer surface [9-11]. The latter method has also been reported to reduce occlusion-based interference effects.

Sampling errors have also been reduced by measuring the volume of solution after its deposition. This measurement has been accomplished by incorporating into the sample solution a small amount of organic solvent as an internal standard [4]. Absorbance at a wavelength appropriate for the particular solvent is then monitored during the drying stage, and is proportional to the volume of solution originally deposited.

Changes in resistance in a tungsten loop atomizer [12] have also been used to signal the end of sample evaporation. The volume initially applied can then be determined from the duration of this drying step.

In the present study, a device was developed which is capable of reproducibly and repetitively dispensing aqueous samples in the form of microdroplets, approximately 150 μm in diameter. This microdroplet generator (MDG) has been described previously [13] and was applied to the study of sample application in ETA with minor modification. The characteristics of the MDG are summarized in Table 1.

For instrumental convenience, microdroplets are produced approximately 2 cm above the atomizer unit, and fall freely into it; consequently, any problems associated with solution transfer are eliminated. Sample spreading and absorption also are reduced by introducing microdroplets into a preheated atomizer, as is ordinarily done in aerosol deposition [9-11]. This procedure results in immediate desolvation of the sample upon contact with the graphite surface.

In this investigation, it was determined that the MDG is highly efficient in sample utilization and results in better precision (1-2% RSD) than that obtained from manual pipetting methods. Moreover, because the dispensed volume can be varied conveniently and, if desired, automatically, calibration curves can be generated using a single standard.

The sample introduction system will be compared with other methods of application (micropipette and aerosol deposition) with regard to sample spreading and crystal size in the dried sample as well as such practical considerations as efficiency of sample use, compatibility with organic solvents and ease of operation.

Other researchers [14,15] have suggested that some atomization interferences are linked in part to occlusion of the analyte within the sample matrix. Differences in crystal size in the dried sample should then alter the incidence of occlusion and thus result in a change in the amount of suppression observed. Based on these comparisons, the new sample dispenser should offer a greater degree of freedom from occlusion-based interferences than manual pipetting. Two model interference systems, Cl^- on Pb and SO_4^{2-} on Au were examined in the present study under controlled sample deposition conditions to evaluate the importance of this occlusion effect.

EXPERIMENTAL

Instrumentation

The MDG described previously [13] was modified slightly and coupled to a controlled-temperature graphite furnace atomizer (model 655, Instrumentation Laboratory, Inc., Wilmington, MA). Both peak and integrated absorbance values were recorded with an automated atomic absorption spectrometer (model

951, Instrumentation Laboratory) equipped with single-element hollow cathode lamps (Visimax, Instrumentation Laboratory). These lamps were run at the current recommended by the manufacturer [16]. All measurements were made with deuterium arc background correction. Aerosol deposition was accomplished with a concentric pneumatic nebulizer, spray chamber, and appropriate manifold system (model 254 FASTAC, Instrumentation Laboratory).

For these experiments the MDG was fitted with a modified reservoir system to accommodate smaller bulk sample volumes (100 μ l), and to afford easier sample change. This modified reservoir is shown schematically with the rest of the MDG apparatus in Fig. 1. The reservoir consists of a section of 3 mm I.D. glass tubing with a right angle bend. A 1.6 mm (1/16-inch) wide delivery slot is cut into the forward portion of the tube.

To initiate a dispensing cycle, a peristaltic pump transfers an aliquot of solution into position above this slot, the solution being held in the slot by surface tension. Ordinarily, the solution is pumped slightly past the slot and then moved back in place by reversing the pump to provide a consistent sample location and solution level in the slot. Once the sample is in position, a bimorph-driven drawn-glass stylus (approximately 120 μ m in diameter) reaches through the slot in the reservoir to withdraw and dispense microdroplets from the bulk aliquot. Conveniently, undispensed solution can be recovered by reversing the peristaltic pump.

In the current study, the reservoir was always rinsed with deionized water between samples. However, it would also be possible to alternate sample and wash water "plugs" in an air-segmented stream to reduce sample change-over time. Two 200- μ l aliquots of deionized water were found to be adequate for rinsing of the reservoir.

Other modifications to the MDG system are shown in Fig. 2. These include a screw-adjustable plexiglas mounting seat for the bimorph to allow accurate positioning of the stylus with respect to the delivery slot and a horizontal translator to accurately position the entire assembly over the furnace cuvette for sample deposition. This translator was firmly attached to an adaptor plate to facilitate mounting the MDG to the graphite atomizer housing.

MDG Operation

In operation, the furnace power supply is placed in the manual mode and allowed to reach the temperature selected for sample deposition. This temperature is measured using a tungsten resistance thermometer. The MDG is then slid forward against an adjustable stop to position it accurately above the cuvette. With the sample in place in the reservoir, the gate controller is activated and a preset number of microdroplets are dispensed into the furnace. The MDG is then manually withdrawn from above the atomizer and a cover plate placed over the opening in the adapter plate. Finally, the atomizer is placed in the automatic mode and allowed to execute the remainder of the preset temperature program (i.e. ash and atomize). Operating conditions used for individual elements are summarized in Table 2.

Argon was used to purge the atomizer during all experiments; the flow rate was reduced from the manufacturer's recommended 30 SCFH to 10 SCFH in order to avoid perturbations in the trajectory of the microdroplet stream. This reduction in purge gas flow rate was found not to affect the analytical performance or lifetime of the graphite atomizer.

Conventional graphite atomizer cuvettes coated with pyrolytic graphite were used exclusively. However, the sample introduction opening in the

cuvette was enlarged to 3.0 mm (0.120 inches) to facilitate microdroplet introduction.

Examination of Dried Sample Deposit

Evaluation of sample spreading and crystal size was accomplished by photographing the residue left after deposition of 10 μ L aliquots of 10% NaCl solution. For this study, a 12.7 x 4.8 mm (1/2 x 3/16-inch) section was removed from the center of each graphite cuvette before sample deposition to simplify observation and photographic recording. The results demonstrated here were duplicated in unaltered cuvettes to insure the validity of the results reported. No significant differences were observed.

Interference Studies

The magnitude of a given interference is expressed in terms of percent suppression. These values were determined by calculating the percent change in signal intensity with and without interferent present. Sample deposition conditions were duplicated from the previous studies allowing microscopic observation of deposited material. A general comparison could then be made between crystal size in the deposited material and the degree to which suppression occurred.

Reagents

All sample solutions were prepared daily by dilution of 1000 μ g/mL standard stock solutions (Alfa Products, Thiokol/Ventron Division, Danvers, MA). Deionized water was used for all dilutions and nitric acid was added to all samples to achieve a final acid concentration of 1%.

RESULTS AND DISCUSSION

Optimization of Deposition Temperature

Figure 3 indicates the effect on the absorption (area) signal of furnace temperature during microdroplet deposition. For all elements, the recorded peak area remains constant until about 100°C, the boiling point of the solvent, above which a distinct loss in signal occurs.

Presumably, the deposited sample boils violently upon contact with the heated atomizer at these higher temperatures (> 100°C), resulting in expulsion of a portion of the analyte.

Not surprisingly, the precision of these determinations is also dependent on furnace temperature during deposition, as demonstrated in Fig. 4. As before, the boiling point of the solvent divides two distinct performance regions. Below 100°C the precision remains relatively constant at 0.8 - 2.5% RSD for the elements studied. Above this temperature, precision degrades rapidly. Although precision is always worse at these higher deposition temperatures, specific precision values are not significant and a comparison among the curves for elements listed in Fig. 4 would not be valid.

From these preliminary experiments the deposition temperature was selected to be 90°C for all subsequent studies. At this temperature, the precision of analysis falls between 1-2% RSD, for five replicate samples, superior to that obtained with a 10 µl manual micropipette (3-4% RSD) and comparable to that achieved in this laboratory with a commercial aerosol deposition system (1-2% RSD).

Single Standard Calibration

Electrothermal atomization is inherently a mass-sensitive rather than concentration-sensitive technique. Consequently, it should be possible to

calibrate instrument response in terms of volume (with a constant concentration) rather than concentration (with a constant volume) as is conventionally done. Such a procedure would simplify calibration because only a single standard solution would be required.

Previous attempts to calibrate ETA devices in this manner have suffered from poor precision and nonlinearity [5]. Problems of this type, however, can be significantly reduced using microdroplet sample deposition. Precision is maintained between 1-2% RSD and an accuracy of 5% or better could be achieved for the aqueous copper solutions examined. This improvement is attributed to the reproducible deposition and reduction in spreading of a liquid sample when it is applied as microdroplets to a preheated atomizer surface. In this manner, differences in deposit size and character between large and small volume samples are minimized.

A family of curves illustrating single-standard calibration for copper is shown in Fig. 5. In this experiment, the dispensed volume ranged from 0.6 μl to 20 μl for each of three Cu solutions, having concentrations of 20, 50, and 100 $\mu\text{g/L}$, respectively. Bending observable in the 100 $\mu\text{g/L}$ curve is the result of nonlinearity in absorption measurements made at magnitudes greater than 1.0.

These same data are plotted in a more analytically useful form in Fig. 6. Values in Fig. 6 are plotted on the basis of the mass of copper deposited and should define a single calibration line which is independent of the individual concentration or volume of each sample.

The slight deviation from ideal behavior apparent in Fig. 6 limits the accuracy of this mass-based method to about 5% for masses of Cu between 10 and 900 pg. Curvature apparent above 900 pg copper is the result of customary nonlinearity observed in high absorbance measurements.

Morphology of Dried Sample

In the previous section the practical importance of controlling the spreading of liquid samples at the atomizer surface was underscored. Such spreading, as well as absorption of the sample solution into the atomizer, is significantly reduced when the sample is applied to a preheated atomizer. To facilitate application at elevated temperature, samples should be applied in the form of microdroplets or an aerosol, procedures which enable rapid desolvation without spattering-induced sample losses.

Figures 7-9 indicate typical dried sample deposits obtained after micropipette, microdroplet and aerosol deposition, respectively. Samples from both microdroplets and aerosol were deposited at elevated temperatures, 90° and 130°C respectively, and dried instantly upon contact with the atomizer surface. Deposition in this manner produces a noticeably more uniform and compact distribution of dried sample on the atomizer surface than that produced by micropipette application. The micropipetted samples were added to the atomizer at room temperature, followed by a 20 second ramp to 70°C and 20 seconds at 100°C.

Figures 10-12 show small sections of dried sample from Figs. 7-9 under equal magnification. It is obvious that aerosol deposition (cf. Fig. 12) produces the smallest crystals, appearing like a frost on the atomizer surface. Microdroplets, by comparison, yield a fine crystalline structure (cf. Fig. 11) in the dried sample but one which is noticeably coarser than that produced by the aerosol. Sample deposited with a micropipette (cf. Fig. 10) results in the largest crystals of the three deposition techniques studied. This large crystal size is most likely a result of the slow drying rate necessitated by micropipette application.

Interference Reduction

As shown in Figs. 10-12, crystal size found in dried sample varies with the method of deposition in the following manner: micropipette > microdroplet > aerosol deposition. From the data presented in Table 3, it seems clear that the greatest degree of signal suppression, and thus of interference, occurs when sample is applied with a micropipette, and thus resides in the form of larger crystals at the atomizer surface. The decrease in suppression found with microdroplet and aerosol deposition appear also to follow this trend in crystal size.

In general, a decrease in crystal size results in a decrease in the magnitude of suppression observed. This trend would support an occlusion-based mechanism for the particular interferences studied.

Practical Considerations

Several other factors besides those already discussed are important in the selection of an appropriate method of sample application for ETA. The volume of sample available to the analyst, the importance of conserving the sample, convenience, and compatibility with a given solvent must all be considered.

Microdroplets are dispensed directly from a bulk volume of 100-200 μ l in the reservoir, from which several aliquots can be taken. Moreover, the only limitation to the number of such aliquots is that at least 25 μ l must remain in the reservoir for stable microdroplet generation. Conveniently, even this undispensed portion can easily be recovered by reversing the peristaltic pump, (cf. Fig. 1), making the MDG highly efficient in its use of sample.

In comparison, a micropipette can be operated with a bulk sample volume only slightly greater than the calibrated volume of the pipette. It then dispenses all of its contents.

Both a micropipette and the MDG use sample more efficiently than aerosol deposition. Using a pneumatic nebulizer to generate the aerosol requires that more than a milliliter of solution be available to deposit a 10-20 μL volume in the atomizer. The majority of solution remains behind in the nebulizer spray chamber and is often not easily recovered.

Although the MDG and aerosol deposition are instrumentally more complex than a micropipette, once adjusted they provide high precision with little operator intervention. A micropipette, however, is a relatively simple device yet requires a skilled operator to achieve optimal performance with it. With additional automation, the MDG has the potential to provide unattended high precision sample deposition.

Lastly, solvent compatibility with each device must be considered. Both micropipette and aerosol deposition of organic solvent is possible. However, the MDG is at present not capable of dispensing solutions prepared with an organic solvent, principally because of the reservoir system which is now being used. The relatively low surface tension of organic solvents results in a tendency for solutions made from them to creep through the slot in the reservoir, making reproducible microdroplet formation impossible.

Importantly, working with aqueous and organic solvent mixtures (up to 25% MeOH), is possible with the MDG. Moreover, altering the design of the reservoir, and the material from which it is constructed might make the use of undiluted organic solvents feasible in the future.

Conclusion

Depositing liquid samples in the form of microdroplets has been found to be advantageous in several aspects of ETA. In routine use, better precision is obtained than is possible with a conventional micropipette. Most likely, precision is improved because of the absence of transfer problems and reduced spreading and absorption of the sample at the atomizer surface.

The convenience of electronic control of the dispensed volume allows simplified calibration with a single concentration of standard solution. Lastly, reduced crystal size in the dried analyte results in reduced atomization interferences which are believed to be caused by occlusion of the analyte within the dried sample matrix.

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REFERENCES

1. J. D. Winefordner, Atomic Absorption Spectroscopy, G. F. Kirkbright and R. M. Dagnall, eds., p. 37, Butterworth, London, 1971.
2. F.J.M.J. Maessen, F. D. Posma and Johannes Balke, *Anal. Chem.*, 46 (1974) 1445.
3. C. F. Emanuel, *Anal. Chem.*, 45 (1973) 1568.
4. G. F. Kirkbright and R. D. Snook, *Atomic Absorption Newsletter*, 16 (1977) 108.
5. K. G. Brodie and J. P. Matousek, *Anal. Chem.*, 43 (1971) 1557.
6. K. R. Millar, F. Cookson and F. M. Gibb, *Lab. Pract.*, 28 (1979) 752.
7. V. Sacchetti, G. Tessari and G. Torsi, *Anal. Chem.*, 48 (1976) 1175.
8. E. H. Pals, D. N. Baxter, E. P. Johnson and S. R. Crouch, *Chem., Biomed., and Environ. Instrumentation*, 9 (1979) 71.
9. J. P. Matousek, *Talanta*, 24 (1977) 315.
10. R. Woodriff and G. Ramelow, *Spectrochim. Acta*, 23B (1968) 665.
11. M. Chamsaz, B. L. Sharp and T. S. West, *Talanta*, 27 (1980) 867.
12. L. R. Layman and G. M. Hieftje, *Anal. Chem.* 46 (1974) 322.
13. J. G. Shabushnig and G. M. Hieftje, *Anal. Chim. Acta*, 126 (1981) 167.
14. L. R. Hageman, J. A. Nichols, P. Viswanadham and R. Woodriff, *Anal. Chem.*, 51 (1979) 1407.
15. J. A. Krasowski and T. R. Copeland, *Anal. Chem.*, 51 (1979) 1843.
16. Atomic Absorption Methods Manual, Vol. 2, Flameless Operations, R. H. Emmel, M. Fogg Bancroft, S. B. Smith, Jr., J. J. Sotera and T. L. Corum, Instrumentation Laboratory, Inc., 1976.
17. H. L. Kahn, M. K. Conley and J. J. Sotera, *Am. Lab.*, 12 (Aug., 1980) 72.

Table 1

Microdroplet Generator Operating Characteristics

Droplet size:	150 μm diameter (typical)
Droplet Production Rate:	160 Hz
Solution Deposition Rate:	18 $\mu\text{L}/\text{min}$
Bimorph Driving Voltage:	100 Vp-p
Minimum Bulk Sample Volume:	100 μL
Deposition Volume Range (without air jet deflection system [13]):	200 nL and up

Table 2

Atomizer Operating Conditions

	<u>Cu</u>	<u>Mg</u>	<u>Mn</u>	<u>Pb</u>	<u>Au</u>
Wavelength (nm):	324.7	285.2	279.5	217.0	242.8
Bandpass (nm):	1.0	1.0	0.5	1.0	1.0
Integration period (sec):	5	5	5	5	5
Atomization temp (°C):	2000	2100	2200	1800	1800

Table 3

Effect of Deposition Method on Occlusion-based Atomization Interferences

<u>Deposition Method</u>	<u>Interference of Na₂SO₄ on Au determination (% suppression)</u>		<u>Interference of NaCl on Pb determination (% suppression)</u>	
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Micropipette	90	65	9	42
Microdroplet	85	-	3	-
Aerosol	71	45	9	0

(A) 10 μ L; 25 μ g/L Au, 0.1% Na₂SO₄

(B) 25 μ L; 10 μ g/L Au, 0.1% Na₂SO₄ (from reference 17)

(C) 10 μ L; 100 μ g/L Pb, 0.5% NaCl

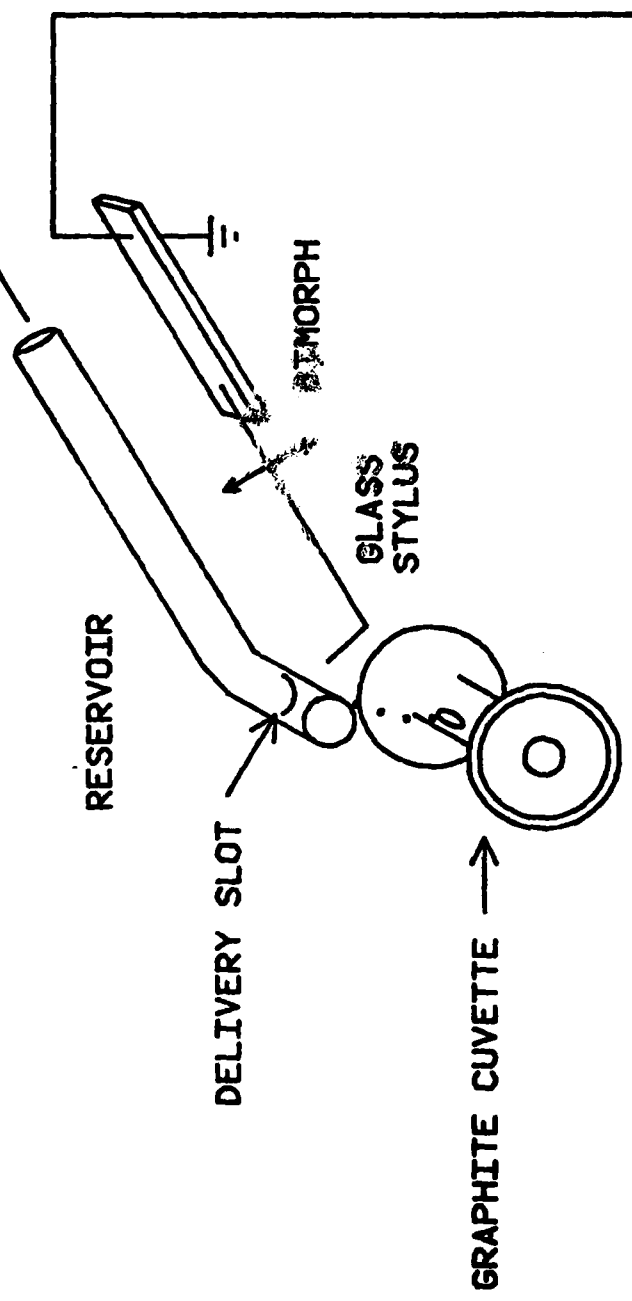
(D) 10 μ L; 100 μ g/L Pb, 0.5% NaCl (from reference 17)

FIGURE LEGENDS

1. Schematic diagram of microdroplet generator sample deposition system.
2. Interface between microdroplet generator and graphite furnace.
3. Effect of deposition temperature (graphite cuvette wall temperature) on atomic absorption peak area. (Cu - 5.4 μL at 100 $\mu\text{g/mL}$, Mg - 3.6 μL at 100 $\mu\text{g/mL}$, Mn - 4.5 μL at 5 $\mu\text{g/mL}$, Pb - 9.0 μL at 100 $\mu\text{g/mL}$)
4. Effect of deposition temperature on measurement precision (relative standard deviation based on 5 replicate samples).
5. Example of single-standard calibration curves with three copper solutions.
6. Single standard calibration data from Fig. 5 normalized for mass of copper deposited. Data points represented by $\odot$ taken from standards at 20 $\mu\text{g/L}$; those designated $\square$ obtained with a 50 $\mu\text{g/L}$ standard; and those marked $\triangle$ for a 100 $\mu\text{g/L}$ standard solution.
7. Photograph of sample within graphite cuvette after deposition of 10 μl of 10% NaCl solution with a micropipette.

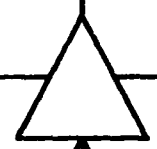
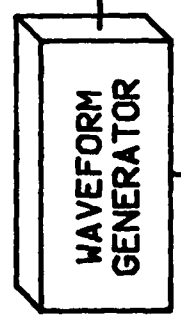
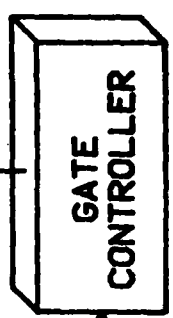
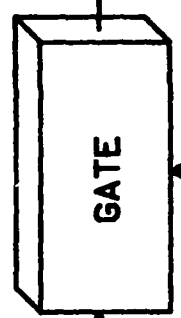
8. Photograph of sample deposit within graphite cuvette after deposition of 10 μ L of 10% NaCl solution as microdroplets.
9. Photograph of sample within graphite cuvette after deposition of 10 μ L of 10% NaCl solution as an aerosol.
10. Photomicrograph of dried NaCl deposit shown in Fig. 7, resulting from micropipette deposition.
11. Photomicrograph of dried NaCl deposit shown in Fig. 8, resulting from microdroplet deposition.
12. Photomicrograph of dried NaCl deposit shown in Fig. 9, resulting from aerosol deposition.

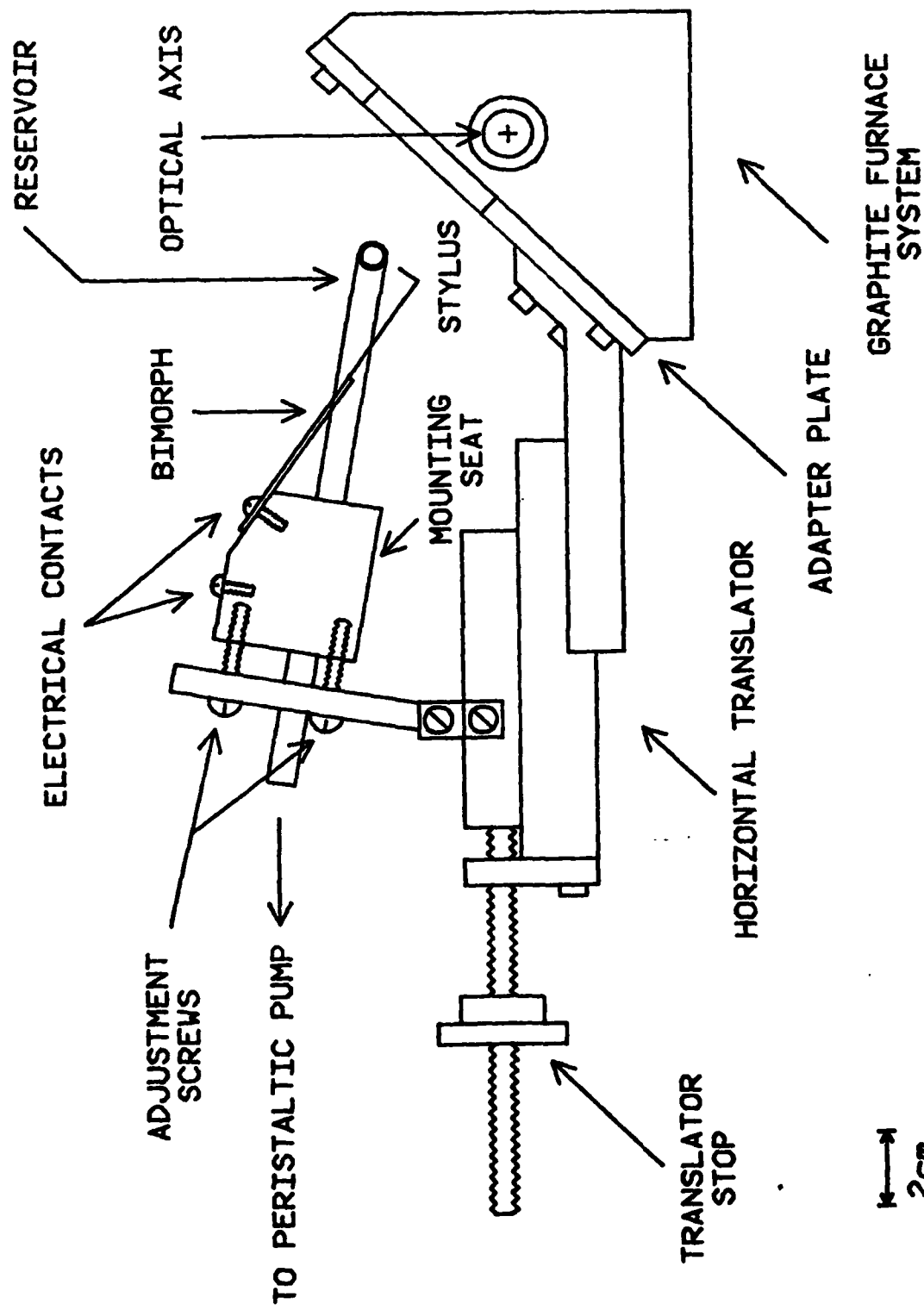
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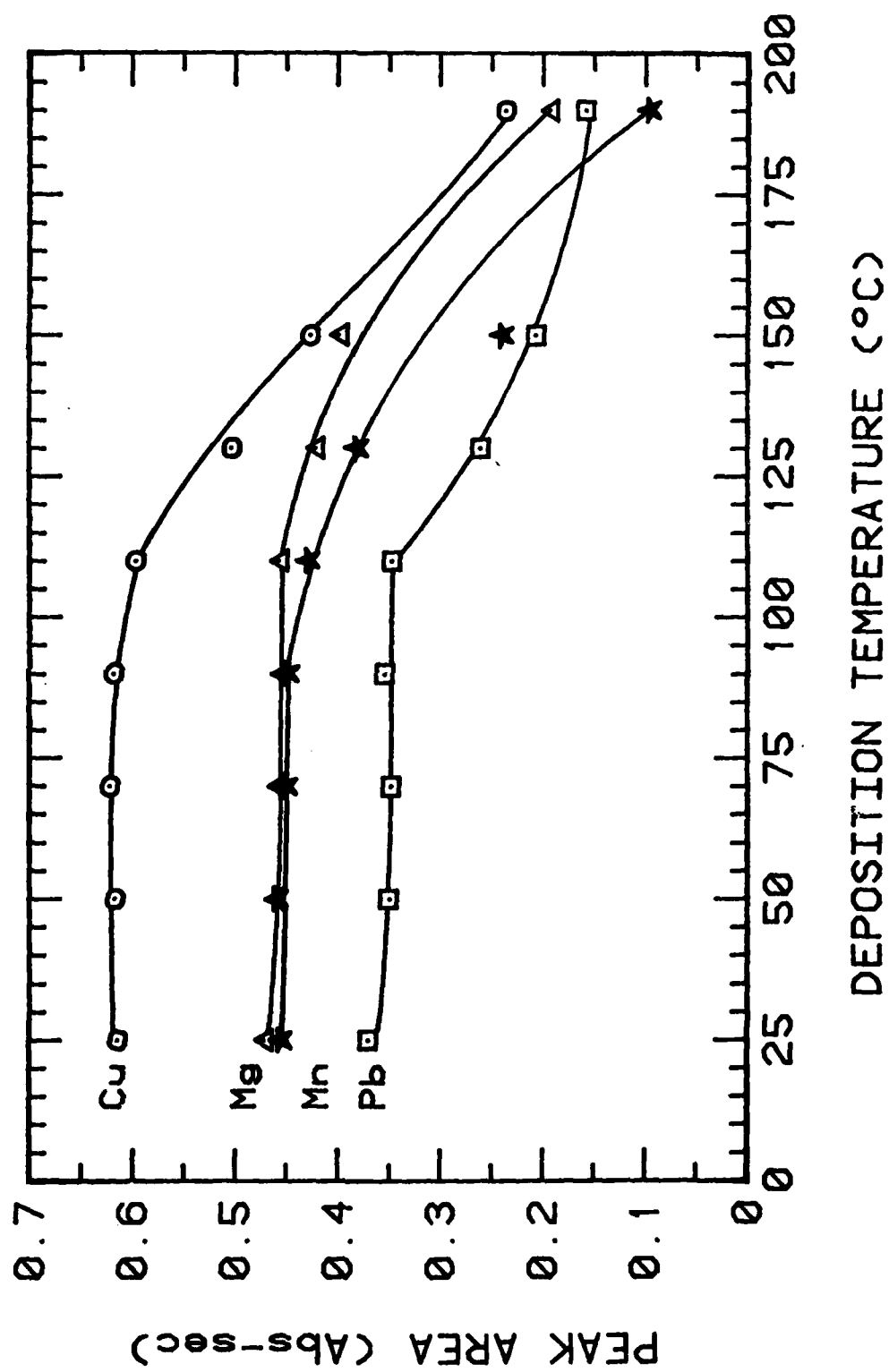


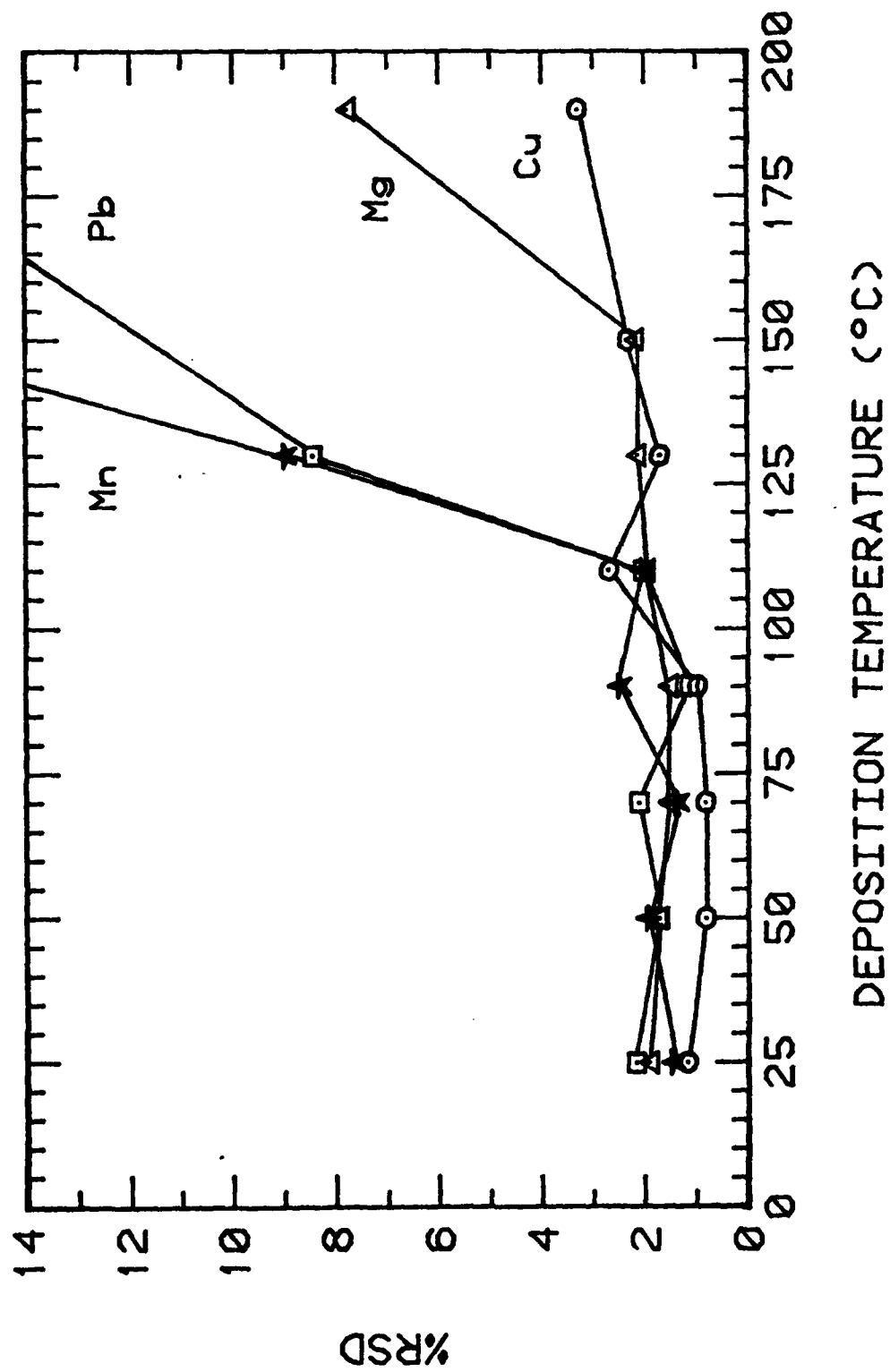
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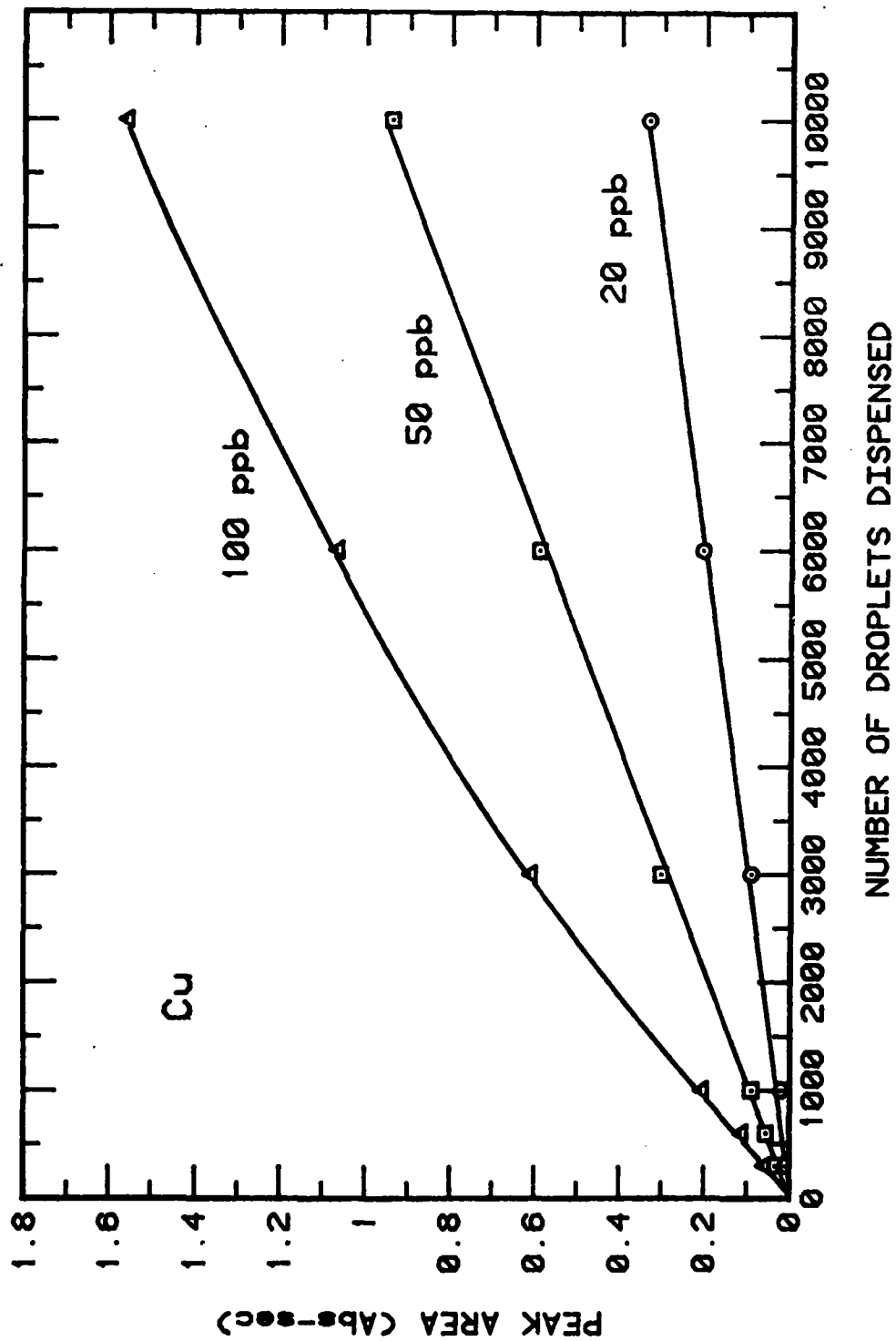
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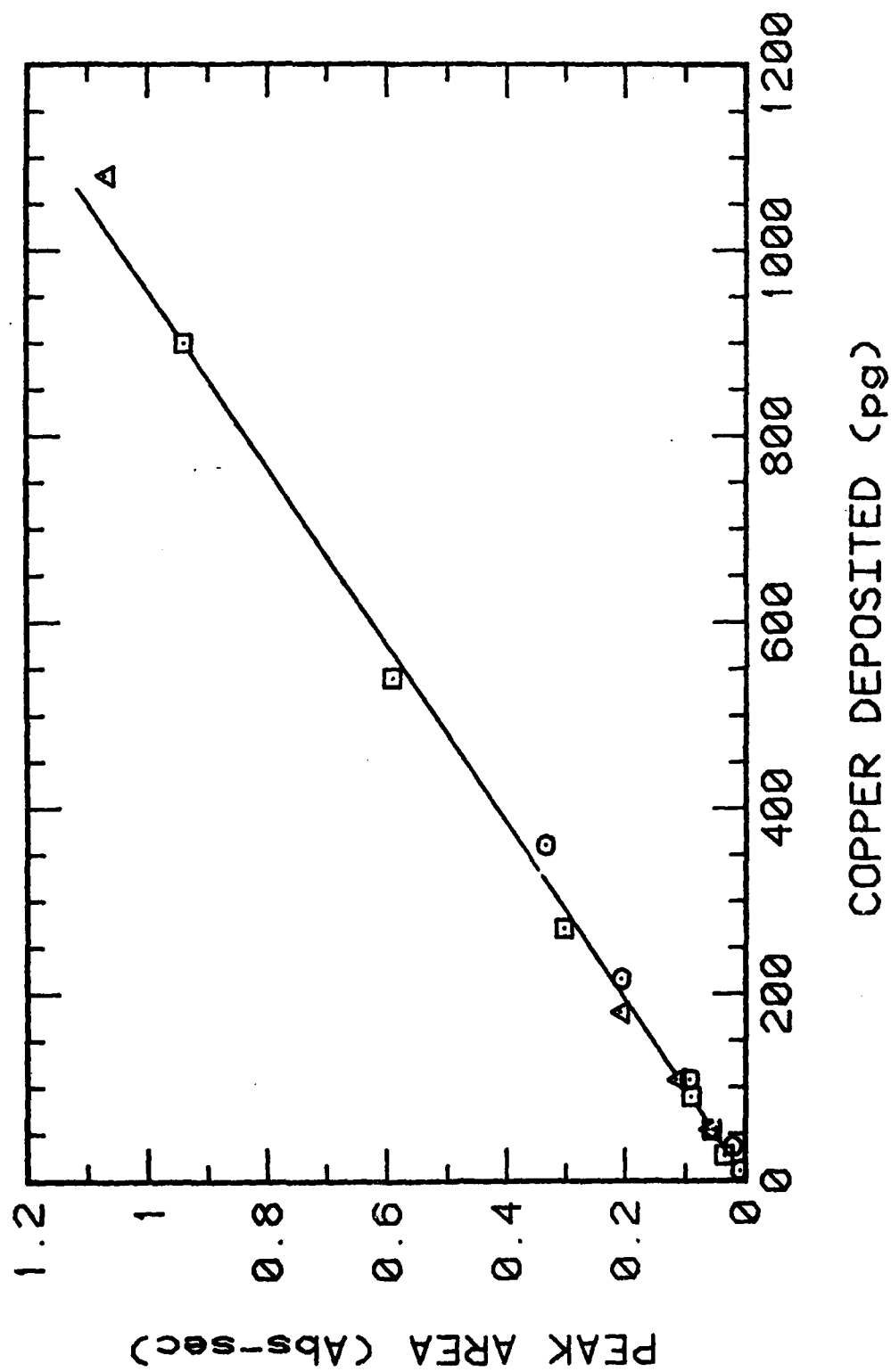


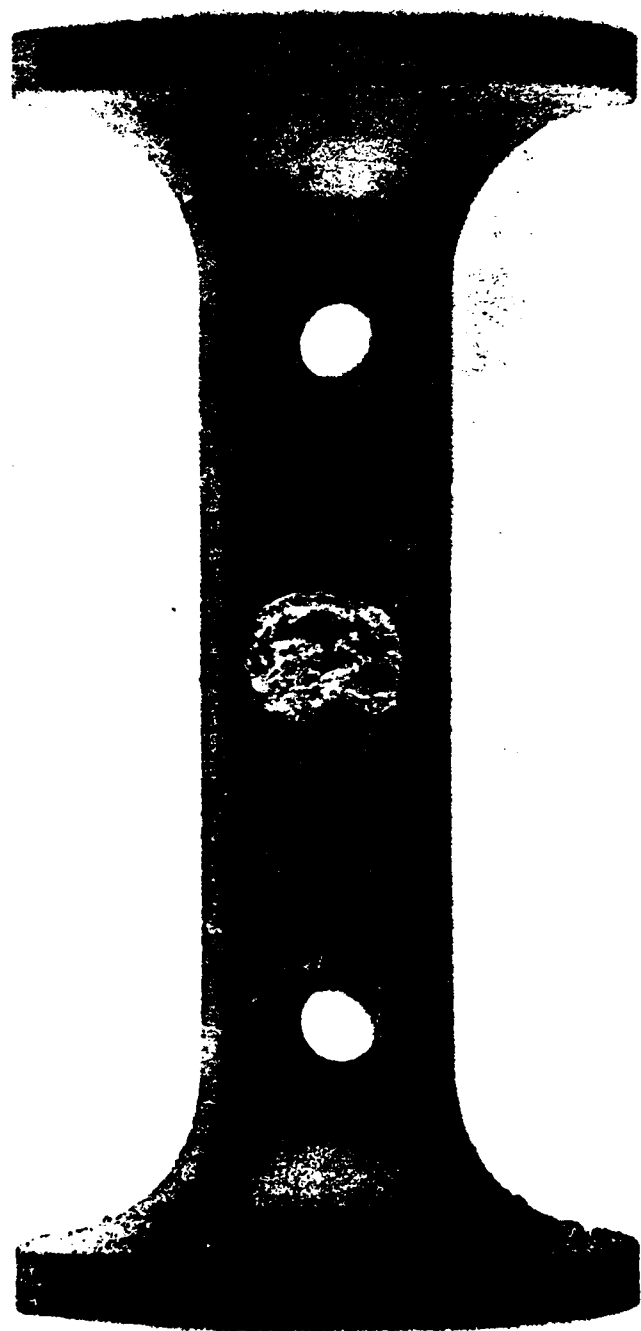


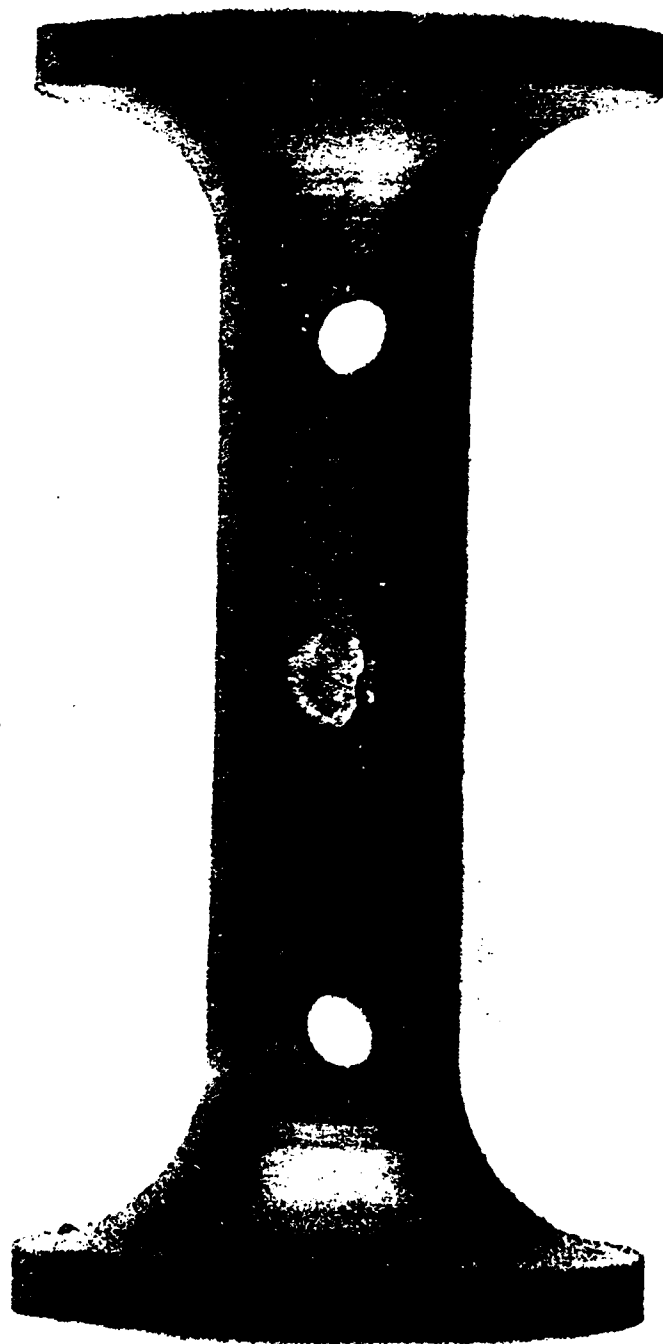


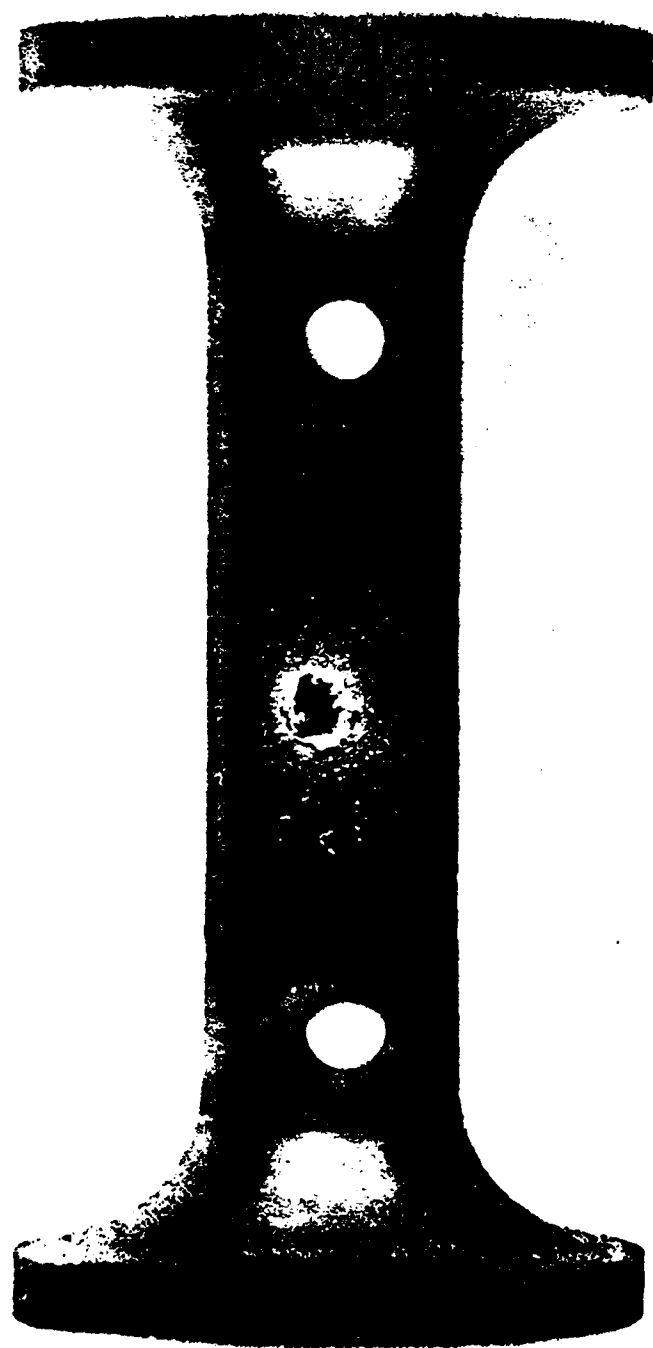










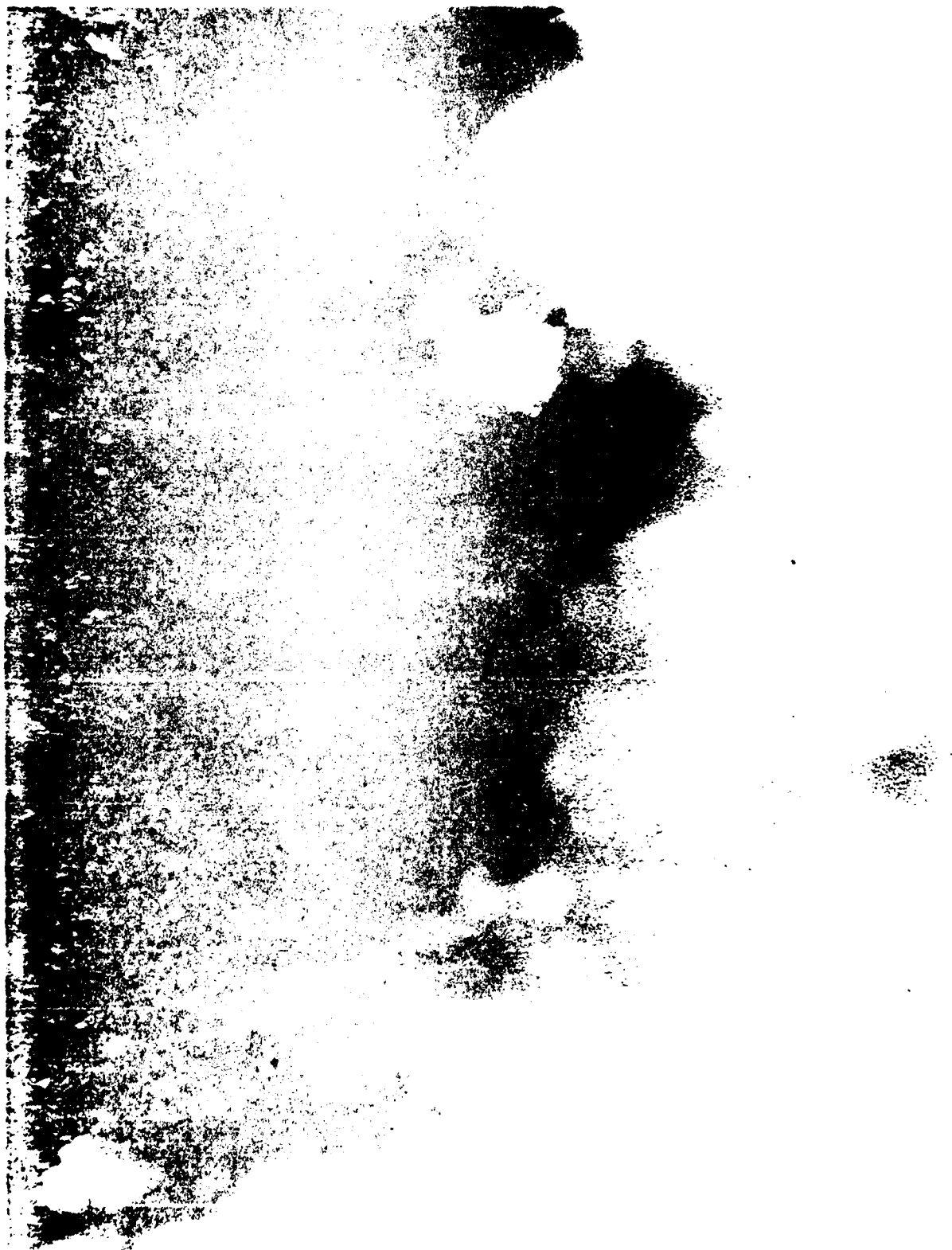




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