DEVELOPMENT OF AN AUTOMATED SAMPLE PREPARATION STATION FOR MICROSAMPLE X-RAY ANALYSIS (MXA)

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ABSTRACT

In Microsample X-ray Analysis (MXA), a droplet of sample—typically 50 microliters—is evaporated onto a thin film sample support substrate and the resulting residue is analyzed for trace elements. In this work we present the development of an automated robotic sample deposition system designed with the goals of improving the uncertainty in residue formation while reducing the drying time to improve laboratory response time. Before implementation on the automated robot, the drying parameters of droplet size, drying method (hotplate or dry flowing nitrogen), drying temperature, and time were explored.

INTRODUCTION

MXA is one of the most sensitive XRF techniques, yielding parts-per-billion detection limits with only minor modifications to existing laboratory instruments. One of the difficulties of this technique is the drying of the sample into a consistent residue. Improvements in support films have helped to ensure that the residue is positioned near the center of the film through use of a mechanical dimple or a hydrophilic treated site [1]. However, the size of the residue is still highly dependent upon the drying conditions and the sample matrix. The most compact residues are obtained by air drying at ambient temperatures, but this causes a delay between sampling and analytical testing. Accelerated drying tends to form rings of sample, with much of the residue deposited outside the field of view of the XRF beam spot (See Figure 1). Earlier work has shown uncertainties in MXA analysis approaching 20% RSD, with most of this variation attributable to lack of precision in the sample drying [2].

Figure 1. Dried residue of 50 μL droplet of multielement standard solution under different conditions. A) 22 C in ambient room air, typical drying time of 5-6 hours. B) 60 C on ceramic hotplate, typical drying time of 1.5 hour. Notice significant fraction of residue in B is outside the central 2 mm hydrophilic site.
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There are several approaches that could be used for heating and/or accelerating the drying of the sample droplet. Some of these are:

- Hotplate
- Dry nitrogen
- Microwave
- Infrared heating
- Vacuum
- Pulsed laser

Microwave drying has proven problematic due to the droplet size being too small to efficiently couple with the microwave radiation. However, the Los Alamos group of George Havrilla has reported success by placing the sample support onto a Weflon platen in the microwave oven [3].

We were also unsuccessful in using an infrared lamp as the heat source as it would heat the supporting frame and begin to melt the adhesive that attaches the film to the frame. Our experience with pulsed lasers was that there was insufficient control to heat the droplet without also melting the sample support film.

Trials with vacuum evaporation and/or freeze-drying yielded good dried residues, but the time for sample preparation was not significantly shorter than drying the sample on a hotplate with slightly elevated temperature. Some other groups report success with vacuum-dried samples [4].

Based on these trials, we elected to use hotplate drying as the primary method in our laboratory. However, one of the purposes of this research project was to explore further the use of dry nitrogen, and particularly heated dry nitrogen, as an alternative to the hotplate drying.

The reasons for automating the sample preparation procedure are quite obvious. Some of these reasons, and design considerations for an automated sample preparation station are:

- Minimize sample dry time
- Improve site-to-site precision
- Minimize cross-contamination
- Remove operator from the process
- Deposit 50 μL or more per sample
- Compatibility with nitric-acid-based samples

The primary goal for this development project was to reduce the sample drying time while maintaining or improving the site-to-site precision. However, as explained above, accelerated drying at high temperatures yields large rings of deposits that are outside the field of view of the beam spot in many XRF instruments. In order for all of the residue to be deposited into a 2 mm site at the center of the sample support film, the droplet size must be smaller than 2 mm. This required that we use droplets of 2 to 3 μL maximum volume. In order to maintain a total sample volume of 50 μL we would need to do replicate depositions on the same film. This paper will report the results of our tests of heated nitrogen as an accelerated drying method, the practicality of using repeat depositions of small sample volumes, and the design and fabrication of a prototype automated sample preparation station.

**DRYING EXPERIMENTS**

To explore the effect of the sample volume on the drying time, a series of samples were dried at high temperature on a ceramic hotplate and the dry times in minutes per microliter were recorded. The temperature limit for the sample support frame is 80 C, so a temperature of 75 C
Figure 2. Drying times as a function of volume on both AP1 and Prolene films. Hotplate dried at 75°C.

It was found that introducing a stream of nitrogen onto the droplet surface would accelerate drying. To test this effect at various gas temperatures a manifold was designed with a cartridge heater to supply dry heated nitrogen. A thermocouple provides feedback to a temperature controller to maintain the nitrogen temperature at a given setpoint. Nitrogen at various temperatures was directed at 2 μL droplets and the dry time in minutes per microliter were recorded. The nitrogen flow rate was 9 liters/min. For comparison, a series of preparations were also performed with the hotplate drying system set at the same temperature as the nitrogen gas. Results are shown in Figure 3.

It is apparent from this data that the flowing dry nitrogen is much more efficient at evaporating the droplet than is the hotplate system alone. This is probably due to better heat transfer from the nitrogen to the droplet, and also due to a reduction in partial pressure of water vapor above the droplet as the vapor is swept away by the flowing gas.

To see if the drying rate could be improved even further by combining the hotplate with the dry flowing nitrogen, several combination conditions were evaluated. These are summarized in Figure 4. The fastest drying conditions were with the heated nitrogen at 75°C. There is very little difference in drying rate with or without the hotplate at 75°C as can be seen in the last two bar chart series. For this reason the heated flowing nitrogen gas without hotplate was chosen as the drying mechanism in the automated sample preparation station. There is very little difference in dry times between 60°C and 75°C, so 65°C was chosen as the standard condition.

Finally, it was left to determine whether repeated depositions of small sample volumes would yield substantially equivalent analytical results to single depositions of 50 μL. Several samples were prepared by evaporating 25 replicates of 2 μL or 17 replicates of 3 μL. (While 5 μL samples...
Figure 4. Various drying combinations using heated nitrogen and a ceramic hotplate. Note that the most significant changes are due to variations in nitrogen temperature. At high nitrogen temperatures there is very little effect from the hotplate, as demonstrated in the last two bar series.

Figure 5. Multiple depositions of small sample volumes dried in flowing nitrogen at 65°C. A) 25 depositions of 2 μL for total volume of 50 μL. B) 17 depositions of 3 μL for total volume of 51 μL.

would dry quicker, this was not considered an option since the residue size is too large.) Photographs of some representative samples are shown in Figure 5. It can be noted that the residues are positioned very well at the center of the films. As expected, the 3 μL depositions are larger in diameter than the 2 μL depositions. XRF measurements with both a 2 mm and 4 mm x-ray tube collimator showed that both residues required the 4 mm collimator for good precision. (See Tables 1 and 2). Beam area on sample with the 2 mm collimator is 2.4 mm by 3.0 mm. Beam area with the 4 mm collimator is 4.0 mm by 5.0 mm.
Table 1. Comparison of 25 depositions of 2 \( \mu L \) each with a single 50 \( \mu L \) control sample using 2 mm and 4 mm collimators. Control sample measured with 4 mm collimator. Differences are probably attributable to variations in pipet calibration. Results show much better precision with the 4 mm collimator.

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|          | mean           | 18.68        | 48.35        |
|          | s              | 9.27         | 3.26         |
|          | %RSD           | 49.59        | 6.75         |

Table 2. Comparison of 17 depositions of 3 \( \mu L \) each with a single 50 \( \mu L \) control sample using 2 mm and 4 mm collimators. Control sample measured with 4 mm collimator. Differences are probably attributable to variations in pipet calibration. Results show much better precision with the 4 mm collimator.

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|          | mean           | -1.48        | 36.15        |
|          | s              | 3.79         | 4.97         |
|          | %RSD           | NA           | 13.75        |

AUTOMATED STATION SETUP

The automated sample preparation station required an X-Y mechanical robot assembly with the ability to aspirate and dispense 2 to 3 \( \mu L \) volumes. The X-Y robot tested was a Gilson model 223 sample handler. The handler was interfaced with a Gilson model 402 syringe pump with 100 \( \mu L \) syringe. This equipment is shown in Figure 6.

To position the sample, the test tube racks underneath the probe arm on the 223 sampler were removed and a platform was built in their place. The platform has a movable drawer for loading several sample support frames and positioning them for automated deposition. In order to introduce the heated nitrogen onto the surface of the droplet, it was necessary to design and build
a special gas delivery manifold. This manifold is detailed in Figures 7 and 8. The sample droplet is deposited through a thru-hole in the manifold. Nitrogen gas is delivered into a series of serpentine baffles that heat it to the desired temperature using cartridge heaters embedded into the metal block of the manifold. Heated gas is channeled into the gas delivery manifold, where it moves through a chamfered orifice onto the surface of the droplet. The chamfer is designed to introduce the gas flow in a conical shape, equalizing the gas pressure on the surface of the droplet and minimizing movement of the droplet under the flowing gas. Earlier designs with only a single gas orifice tended to disturb the droplet position with uneven forces and turbulence.

CONCLUSION

With this automated station it is possible to deposit multiple replicates of sample solution onto the same site on a sample support film and dry each droplet rapidly to minimize sample preparation time. Previous preparation schemes with air drying required 5 to 6 hours in low humidity environments to dry 50 μL samples. With the automated station the same 50 μL total volume can be deposited as 25 replicates of 2 μL each, and the dry time is reduced to below 1.5 hours. It is believed that this “convection oven” approach will be independent of the ambient laboratory humidity, but this is yet to be shown in practice.

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REFERENCES


