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SAMPLE POSITIONING EFFECTS IN
X-RAY SPECTROMETRY

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ABSTRACT

Instrument error due to variation in sample position in a crystal x-ray spectrometer can easily exceed the total instrumental error. Lack of reproducibility in sample position in the x-ray optics is the single largest source of system error. This paper describes the factors that account for sample positioning error and many of the details of flat crystal x-ray optics.

Current technology allows the instrument manufacturer to offer x-ray spectrometer systems that are capable of great sensitivity and reproducibility. Much of this refinement in the instrument in terms of sensitivity and reproducibility has been brought about in the last five or six years. If one compares specifications of present day systems with systems of five years ago, one finds that we can see an across-the-board doubling of intensity. In the case of low atomic numbered atoms such as aluminum, magnesium and sodium the intensity from a given standard may have increased by an order of magnitude.

Equally important, the system stability has greatly improved. Five years ago we talked about total system reproducibility in terms of tenths of a percent. Present specifications on spectrometer systems are now in the range of a hundredth percent. Thus we can talk in terms of an order of magnitude improvement in this area.

These rather dramatic improvements in x-ray systems have come about for a variety of reasons: ultra stable generators, improved x-ray tube design, improved optics, anode to sample coupling distance, better crystals, temperature stabilization of crystal chamber, gas density compensation, better detector design and better electronics. Indeed the system has been improved and refined in every subsystem.

It hardly needs to be mentioned that these rather great improvements are accompanied by large increases in dollars. These systems have doubled in price and now range from \$80,000 to well over \$100,000.

This case for x-ray spectrometers can be applied to most other areas of instrumentation as well. For example in the areas of electron optics, mass spectrometry, and infra-red spectroscopy equally startling advances have been made.

The reason for this discussion as a preamble to my talk on the importance of sample positioning is two fold.

(1) The effects of sample positioning on current generation instruments is of much greater significance than it has been on previous generations. This is so because the improved performance of the instrumentation is better able to reveal irregularities in sample position or for that matter any other operational maladjustments than it ever has been before. Furthermore, it is implicit that industry is going to take full advantage of these improved instruments in terms of lower detection limits and tightening up of analytical spreads. Thus these irregularities will most likely manifest themselves in the form of poor data.

(2) The second point I would like to make concerns itself with the total system performance. My varied experience in not only x-ray spectroscopy but other types of analytical instrumentation brings me to the conclusion that the scientists in charge of these systems are going to have to become much more conscious of total system performance. My travels to various laboratories around the country have revealed that there is a very large range in system performance. In some cases I have seen situations where very expensive equipment is idle simply because it doesn't give good data and the laboratory has invested thousands of dollars attempting to make it work with little or no success.

I believe I can tell you the reason this has happened. It is simply due to the accumulation of a number of seemingly minor problems which are most likely unnoticed by the casual observer. These systems are very complex and the type of malfunctions we are talking about are subtle. Unfortunately a number of these problems can phase together to manifest themselves into an easily discernable problem that even the manufacturer has difficulty solving.

Unraveling problems of this sort can be very tedious and time consuming since they tend to be masked in the total system statistics. This can be an insurmountable task if the laboratory has not generated any records of past statistical trends. Most scientists tend to think in terms of catastrophic failure.

I believe it is the duty of the scientists in charge of these systems to configure some experimental design that allows a comprehensive statistical analysis of the total system with some method of extracting the statistics of the various sub-systems such as the sample positioning system, the x-ray tube, the high voltage and the electronics. With this technique, the operator can easily spot and locate problems as they arise.

Figure 1 justifies what I have proposed. Depicted are intensity data taken from four systems of identical configurations. These four systems are in four laboratories across the country. A copper standard was used and identical conditions were dialed onto the systems. Each 2θ line was peaked for maximum intensity.

Instruments manufacturers generally expect instruments of like configuration to agree within 10%. Figure 1 shows data taken from instruments W, X, Y, and Z. Under each of the three two theta values are sets of numbers ranging in the thousands. These numbers are dimensioned in counts per second and represent intensity measurements for that particular 2θ value on the indicated instrument and the indicated detector. The numbers in parentheses are figures of merit relating how that particular count rate compares to the largest count rate in the column. The average value represents a figure of merit of the total instrument.

These happen to be four instruments out of a dozen that could be mentioned that show similar spreads.

2θ VALUE

INSTRUMENT	40.46	45.03	99.99	AVERAGE
W	8,200 (.46) 22,950 (.47)	39,300 (.49)	5,500 (.66) 18,900 (.82)	.59
X	15,650 (.88) 40,200	72,965 (.91)	7,226 (.87) 22,408 (1)	.90
Y	17,775 (1) 48,712 (1)	79,910 (1)	8,275 (1) 21,778 (.97)	.99
Z	10,500 (.59) 25,299 (.52)	44,350 (.55)	5,866 (.71) 19,856 (.89)	.61

The average value is arrived at by taking the average % of maximum count for a given instrument.

Scintillation c/s (% Maximum et)
Flow Counter (c/s) (% of Maximum)

Experimental Design - Since the purpose of this talk is not to discuss total instrument error, but rather only sample position error, we will mention the experimental design only in passing. Figure 2 depicts the expected errors for a typical x-ray spectrometer.

SOURCE OF ERROR	VALUE %
(a) Typical Total System Error	
1-Multiple Element (Ratio Method)	0.4146
2-Single Element (Absolute Method)	0.5831
(b) Equipment Error (Sample stationary in x-ray analysis position)	
1-Short Term (1 Hour)	0.0532
2-Long Term (4 Hours)	0.2007
(c) Counting Error	0.0707
(d) Sample Changing Error - Total	0.3089
1-Retracton/Insertion	0.0546
2-Placement of Sample	0.0773
3-Sample Holder Differences	0.2940
(e) Sample Difference Error	0.1693

Item d is the category of interest and as a consequence deserves some elaboration.

The total sample changer error is defined as the summation of all errors that are generated by the act of changing samples, positioning the sample in its holder and differences in sample holders. The data was taken on the same sample each time.

The total sample changer error of 0.3089% is considered a bit high, but this data was taken with a universal sample changer designed to accomodate 32 samples rather than the two or four normally expected. A sample error of somewhere between 0.2% to 0.25% would be expected on a spectrometer of standard configuration. This sacrifice in stability was made in order to process greater numbers of samples.

Since the total sample changer error is a major component of the total system error, it is important that the investigator keep a close check on this parameter in order to maintain the total system stability in specification. At this point we shall review some of the sensitive features that determine the sample position error.

The flat crystal x-ray spectrometer is typically configured as shown in Figure 3.

In regards to sample position effects, the important thing is the relationship between the x-ray tube and the sample and the sample and the first collimator. The following condition must prevail:

The distance between the x-ray tube effective focal spot and the sample must be short enough to assure that the area of view by the first collimator is slightly larger than the area of illumination of the x-ray tube by the sample. This is generally deemed to be the most critical portion of the optics and is approximately set at 25-30 mm. The shorter this distance, the greater the intensity.

Figure 4 depicts the configuration of the x-ray tube anode relative to the x-ray tube window.

FIGURE 4 X-RAY TUBE CONSTRUCTION DETAILS

The area on the anode that the electron beam impinges on is called the focal spot. The focal spot (with a finite depth) is the source of x-rays from the tube. In general, the amount of power one can apply to the x-ray tube is determined by the focal spot size. The larger the focal spot size, the greater the power. In this instance, the area of the focal spot happens to be 4 mm X 10 mm.

On the other hand, it is desirable to have the x-ray source approximate a point source. This is accomplished by taking advantage of the geometry of the anode relative to the x-ray tube filament and the window or sample.

Since the anode is tilted 30° away from normal to the long axis of the x-ray tube, it is possible to view the focal spot at an angle. Thus we have what is called in x-ray tube technology an effective focal spot size. If one works out this trigonometric relationship, the effective focal spot size turns out to be almost 5 mm (instead of the 10 mm) by 4 mm. Notice there is no fore-shortening in the 4 mm direction. Thus, a view normal to the x-ray tube window gives an effective focal spot size of approximately 4 mm X 5 mm.

Figure 5 shows that the x-ray tube window is not parallel to the sample surface, but rather tilted at an angle of approximately 50° . Thus the effective focal spot size is slightly different than the 4 mm X 5 mm mentioned above and turns out to be ~ 3 mm X 5 mm.

The x-ray source is thus a point source and the x-ray flux density as a function of effective focal spot - sample separation follows an inverse square law as shown in Figure 6.

Figure 5

$$I_2 = I_1 \frac{D_1^2}{D_2^2}$$

E.G. AN INCREASE OF 4 MM (27 MM TO 31 MM)
WILL CAUSE A LOSS OF INTENSITY OF 29%

Figure ~~XI~~ 6

INVERSE SQUARE ~~RELATIONSHIP~~ Relationship

Figure ~~XI~~ 6

When one considers the inverse square relationship it is easy to see why sample-focal spot coupling is critical to x-ray intensity. For example if one changes the distance from 27 mm to 30 mm one would expect the flux density to decrease by 29%. One should keep in mind that the total x-ray flux will remain unchanged, (neglecting scatter in the intermediate path). It is the x-ray flux per unit area that will change. Since the x-ray optics, the collimators, crystal, and detectors place a limit on the maximum area of the sample that is examined this factor can be very critical. Figure 7 shows a plot of the intensity change as a function of sample displacement from an ideal position of 27 mm. This so called ideal 27 mm is an optimum figure set by geometrical constraints of locating the x-ray tube as close as possible and yet having a reasonable angle of view by the spectrometer optics. It should be noted that a displacement of .001" will result in a 0.188% change in x-ray flux density.

Going back to Figure 2 you may recall that the total error we look for in regard to sample positioning error is something on the order of 0.3%. Figure 7 demonstrates that a displacement of only .002" is all that is needed to exceed this expected error. For those of you that don't have an appreciation of inches graduated in thousands, a human hair is on the order of 0.002" in diameter.

We mentioned earlier that the inverse square relationship is not the only factor that must be dealt with when one considers the effects of positioning a sample. It is time to consider the super position of the projected x-ray spot and the projected x-ray optics sighting hopefully at the surface of the sample.

Figure VII 1 % CHANGE IN X-RAY FLUX DENSITY AS A
function of SAMPLE-FOCAL SPOT DISTANCE

Each 0.001" will result in a 0.188 % change

~~Sketch~~ #7

Figure VII 7

Figure 8 depicts a cross-section of the x-ray optics, sample, and x-ray tube. For simplicity, the rays emitting from the four corners of the x-ray tube focal spot are projected onto the sample surface. The drawing is to scale and the focal spot to sample distance is 27 mm.

A penumbra results from the finite focal spot size because, (as seen in Figure 8), points on the periphery of the specimen cannot see the entire focal spot.(1)

The collimator is also shown in Figure 8 and the dotted lines projected to the sample surface represent the area of view of the optics on the sample surface. Thus the surface of the sample must lie in an imaginary plane in the spectrometer such that the spot projected from the x-ray tube and the spot viewed by the collimation system overlap. Maximum intensity is registered by the detector system when the optical system is centered on the x-ray spot projected on the sample surface. Since these two areas are approximately equal, displacement of the sample from an imaginary plane where the above conditions prevail is going to cause a reduction in intensity. As the sample is moved away from the x-ray tube, the x-ray spot on the sample will sweep away from the center of the sample toward the collimator side. If the sample is lowered, the spot will sweep in the direction of the x-ray tube. Since the collimator system is fixed in position to view the center of the sample at a specific height, the collimator will not be able to view the total source of x-rays emitting from the sample unless the optics, the sample, and the x-ray tube are on centers. If the x-ray tube were facing the sample such that the center of the x-ray beam impinged on the sample surface at 90° , the intensity distribution across the sample would be uniform from one side of the sample to the other side. That is to say, if one picked a point a certain distance away from the center of the sample toward

the collimator side of the sample and took a measured intensity, one should be able to go the same distance away from center on the side away from the collimator and measure the same intensity. Thus there should be a point for point agreement in the intensity distribution on both sides of the sample.

Unfortunately, because of geometrical limitations, it is not practical to arrange the tube as mentioned above, but rather, the tube must be tilted at an angle of approximately 50° .

Figure 8 shows intuitively that along the optic axis there would be a non-uniform distribution of x-ray intensity across the sample surface. In addition, Figure 8 points out the section of the area viewed on the optic axis center. The dotted lines define this section.

The experimental determination of this distribution consisted of taking a number of two inch diameter copper disks and drilling 1/16 inch diameter holes at specified distances from the center of the disk. Each disk was loaded into the spectrometer and the hole aligned on the optic axis. A fixed count was taken on a copper line, and the same procedure was repeated until the measurements were made at 1/16 inch intervals across the sample surface. Figure 9 shows a plot of these results.

Calling our attention to the edge nearest the x-ray tube, the x-ray intensity drops off rather rapidly. This rapid drop off comes almost at the edge of the area of the sample viewed by the collimator. Thus, cropping on this side of the sample surface will have an immediate effect of dropping the intensity rather precipitously. This effect would be noticed if the sample were raised. Fortunately, this situation is not very easy to achieve since one would have to change the sample height some .075" to realize this condition.

If we now consider the collimator side of Figure 9, we notice that the intensity across the sample rather slowly drops off from 100% at the maximum to 99% at the collimator boundary. It is this effect that one must deal with when considering intensity changes as a function of sample position. Again, it should be noted that the rapid tailing off beyond the collimator boundary is not observed until the sample is moved a relatively large distance; approximately 0.125". This effect is observed when the sample is lowered.

The portion of the curve in Figure 9 of most concern is the portion in the mid part of the curve. Lowering the sample will cause a gradual loss in intensity as the area the collimator views moves toward the collimator side of the sample.

In order to obtain experimental values of intensity versus sample height, a gauge graduated in 0.001 inch increments was built. This gauge was placed in a sample cell and counts versus sample height were made. Figure 10 shows the results of these measurements.

As mentioned earlier, all of the above assumes a sample of high absorption for x-rays. It assumes that the x-ray interaction is strictly a surface phenomena. In actual practice, this is seldom the case. Samples range from the very high absorbers such as is found in metallurgical materials, to intermediate absorbers such as powders, and to low absorbers such as liquids.

Figure 11 depicts a hypothetical sample exhibiting some absorption. This Figure is intended to demonstrate that the x-ray emission is really from some volume located at some finite depth within the sample.

Figure ~~X~~⁹ Profile of X-RAY INTENSITY ACROSS SAMPLE SURFACE
IN THE DIRECTION OF OPTIC AXIS

DISTANCE FROM CENTER OF SAMPLE (INCHES)

Figure ~~X~~⁹

Figure ~~X~~¹⁰

-20-

Relative Intensity vs. Mil's displacement
2" diameter sample - solid line
1.25" diameter sample - dashed line

Figure DEPTH OF PENETRATION OF PRIMARY RADIATION
AND DEPTH OF SOURCE RADIATION

In addition, this figure illustrates that the excited x-ray must travel through the sample before emerging from the sample and passing down the collimator. Thus the effective sample height will vary slightly according to the energy of interest and the absorption characteristics of the sample. Fortunately this variation is somewhat less than the problems we have discussed earlier. This situation can for all practical purposes be considered to be a constant when considering samples with similar matrices or at least it can be accounted for.

The liquid sample deserves some special consideration. Liquid samples must be contained by a plastic window on the analysis surface of the sample cell. This surface is often likely to either bow out or bow in and the sample surface has a tendency to curve. Fortunately cups that hold these samples are reduced in size and are most often small enough in diameter that they fall well within the cone of radiation emitted by the x-ray tube. This eliminates any cropping effects caused by sample displacement. Also, the absorption effects on these samples are relatively low and the source of emissions from the sample are from a rather large volume. These points coupled with the consistency of matrix absorption from sample to sample tend to minimize errors.

It has been the writer's experience that the greatest problems associated with liquid cell operations are:

1. For quantitative analysis, a sample must have an infinite depth, or known thickness. In many cases this is difficult to achieve.
2. A problem that can be controlled is volume change due to sample heating in the x-ray beam. The sample cell should not be left in the analyzing position for an excessive time. Also, if the cell ruptures, the operator is left with a mess to clean up.

In conclusion, sample positioning effects can be the source of very significant errors in quantitative analysis. As mentioned earlier a displacement of a sample from its normal position by 2×10^{-3} inches can cause a significant error.

The error introduced by faulty sample positioning is a composite of two factors.

1. Moving the sample away from the x-ray source will cause a reduction in intensity due to the inverse square relationship.
2. Moving the sample toward the x-ray tube will cause the collimator to crop the x-ray source on the sample.

The result of these two effects is an asymmetrical bell-shaped curve that peaks at the correct sample position.

The scientist in charge of an x-ray system should always be aware of the various instrumental error parameters especially sample position. All sample cells and holders that are used should be evaluated on some sort of schedule to insure that the errors are within limits.

The investigator must be aware of the presence of dirt, corrosion, or mylar films around the sample cell and support mechanism.

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