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DENSITY METER ALGORITHM AND SYSTEM FOR ESTIMATING SAMPLING/MIXING UNCERTAINTY

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ABSTRACT-INMM ANNUAL MEETING 1986

The Laboratories Department at the Savannah River Plant (SRP) has installed a six-place density meter with an automatic sampling device. This paper describes the statistical software developed to analyze the density of uranyl nitrate solutions using this automated system. The purpose of this software is twofold: to estimate the sampling/mixing and measurement uncertainties in the process and to provide a measurement control program for the density meter. Non-uniformities in density are analyzed both analytically and graphically. The mean density and its limit of error are estimated. Quality control standards are analyzed concurrently with process samples and used to control the density meter measurement error. The analyses are corrected for concentration due to evaporation of samples waiting to be analyzed. The results of this program have been successful in identifying sampling/mixing problems and controlling the quality of analyses.

INTRODUCTION

Satisfactory mixing of uranyl nitrate has been a concern of the Laboratories Department at the Savannah River Plant. Uranyl nitrate is stored in a large horizontal tank prior to shipment. Recently, the tank's mixing capability has been upgraded with the addition of new mixers. A similar improvement was desired in the ability to screen samples for sampling or mixing problems. A new six-place Anton-Parr/Mettler density meter with an automatic sampler was installed to accomplish this. This paper describes the software developed for data management and statistical analysis of the density information. The sampling situation is reviewed in the next section. The following sections describe the data management, calibration and evaporation corrections, measurement control, and data analysis capabilities of the system.

BACKGROUND

After the tank has been mixed, uranyl nitrate is pumped into a waiting trailer. Six samples are systematically drawn from the filling line and sent to the Laboratories Department for analysis. The samples are combined into two composite samples. The uranium concentration of the solution is determined using the NBL modified Davies and Gray uranium titration method on the composite samples. In addition to the concentration measurements, density measurements are made to determine if problems in sampling or mixing exist. Density measurements are made in duplicate on each of the six original samples. Since the density of uranyl nitrate can be expressed empirically as a linear function of uranium content and free acidity of the solution, the density measurements provide a fast and reliable approach to describe mixing problems. Thus, if the density significantly varies from sample to sample, we can infer that the tank contents have not been well-mixed.

The aim of the density analysis software is to automate data management and data analysis capabilities in a simple streamlined format. To perform density measurements on uranyl nitrate, the operator readies the density meter, prepares samples and places the samples in the sample holder. Then the operator addresses the software by supplying program parameters. The remainder of the operation is fully automatic, freeing the operator for other tasks. The analysis consists of analytical and graphical interpretation of the density data. Additionally, the software automates calibration and measurement control functions, searches for non-typical analytical results, and corrects for concentration due to evaporation loss while samples are queued in the automatic sampler. Automatic rejection of outlying data values is avoided, since it is sound practice to investigate the reasons for non-typical data. However, after investigation, the software permits the analyst to redo the data analysis of production samples without a non-typical result.

The algorithm is written in BASIC programming language. It is implemented on an inexpensive Epson HX-20 computer with a memory expansion module. Data are transmitted from the density meter to the computer through a serial interface. Messages to the operator are displayed on a four by twenty character screen. Results are written to a built-in twenty-four column printer.

DATA MANAGEMENT

The data management portion of the density meter software has two functions. It accepts user input of program parameters and manages the information transmitted by the density meter. The user supplies the program parameters through a series of screen prompts prior to measuring densities. Thereafter, the density meter data is received and analyzed automatically without operator assistance.

The user supplied parameters identify the user, the shipment, and specify additional information such as the acidity of the solution and the density of air and water. A series of menus prompt the operator to enter the necessary information. To illustrate, Figure 1 depicts menus to input the user's identification number. Each menu begins with a prompt and default value. The previous identification number becomes the default response (underlined). The operator either hits enter to choose the default value or overtypes the default value with his or her identification. If a new response is entered, the computer prints the response on a second menu and the user must acknowledge the correctness of the response before proceeding. Occasionally, an inadmissible response is entered, such as a name when a number is requested. Where possible the algorithm checks the admissibility of the response. If inappropriate, a "wrong key" message is printed and the original menu reappears to prompt a new response.

FOUR DIGIT USER ID? 1234 CHANGE NOW OR HIT RETURN	USER ID IS 1234 IF OK= HIT RETURN R= TO REDO
Menu to Log in User ID	Use Verifies Response

FIGURE 1. Prompts Aid User Input.

The second function of the data management portion of the software is to receive, transform, and store information sent by the density meter. Figure 2 illustrates these activities.

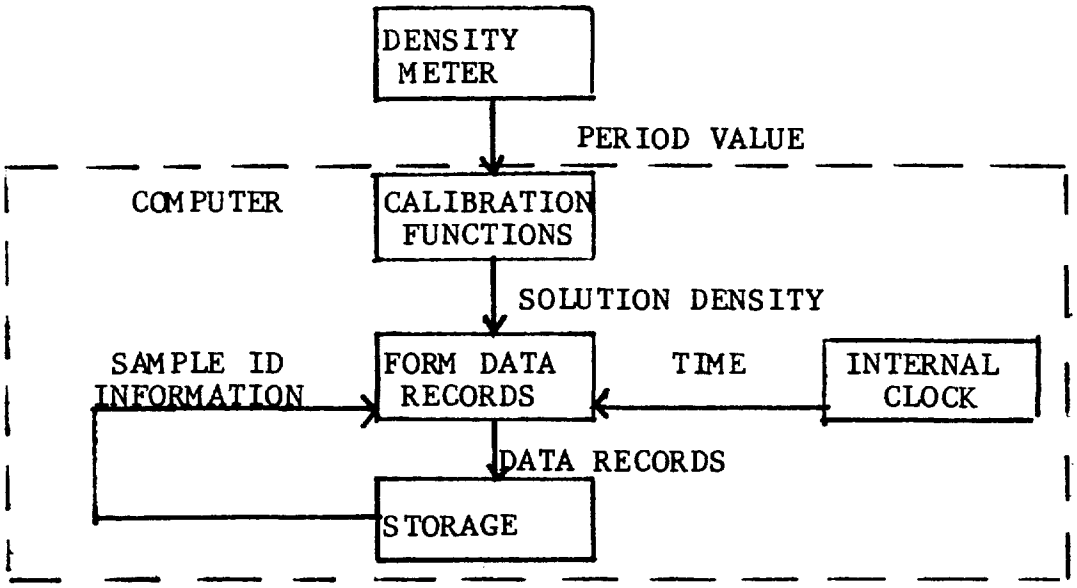

FIGURE 2. Information Flow of Density Data

The density meter is coupled with an automatic sampling device. Once the aliquots are prepared and placed on the sample holder, the user is free for other activities. Each analysis takes approximately five minutes. The density meter analysis of the sample measures the period of oscillation of a vibrating tube. These period values are transmitted automatically to the computer where they must be converted to density values.

The first two period values are for air and water samples. These are used for calibration. Once calibrated, quality control and production samples can be analyzed. The computer receives a period value of a sample solution from the density meter and calculates the sample's density from the calibration function. Then a data record is formed for each density value. This record includes sample identification information previously stored in the computer's files and the measurement time read from an internal clock.

Density measurements are performed on various types of samples. The purposes of taking various types of samples differ and the data must be managed accordingly. Each data record must identify the type of sample as well as store the value of the density measurement. Figure 3 depicts typical records for various types of samples. Production samples are those samples drawn from the trailer filling line. Each of these samples are numbered consecutively; the type designation refers to this sample number. Quality control samples are analyzed concurrently with production samples for measurement control purposes. These samples are labeled 'Q'. Air and water samples are identified by 'A' and 'H', respectively. Samples of quality control standard, water, and air are also used to flush the cell. They are referred to as dummy samples and designated 'D'.

Shipment #	SAMPLE TYPE	DESCRIPTION
	A	Air Sample (Calibration)
	H	Water Sample (Calibration)
	D	Dummy Sample (Flush Cell)
	Q	Quality Control Sample
1 or 2	1,2,3,4,5 or 6	Production Sample

FIGURE 3. Types of Samples

The data management algorithm can accept the density meter values in any previously specified order. This permits measurements to be run in a randomized order.

CALIBRATION AND EVAPORATION CORRECTION

Air and water calibration samples are analyzed at the start of each session. The relationship between density and the squared period of oscillation is linear. The calculations to determine a linear calibration fuction are routine[1] and, therefore, are omitted.

Samples are corrected for evaporation. The vials which hold sample solution are capped with a teflon plug. The plug has a small hole through which solution can be sampled. After some experience measuring densities, it was determined that evaporation of solution was a problem when vials are queued in the sampling rack waiting for analysis. The evaporation between successive measurements was small, less than one unit in the sixth decimal place. However, this became a problem over the entire set of analyses for a shipment. Consequently, a correction for evaporation is made prior to data analysis. Since the time of each measurement is recorded, the change in density per minute is estimated from data and compared to a previously established rate. The previously established rate is used if the estimate is not significantly different from it.

MEASUREMENT CONTROL

Quality Control samples are analyzed concurrently with production samples to ensure reliable results. A simple summary of results is usually adequate. Figure 4 shows a typical printed summary. The summary is composed of a listing of quality control density measurements plus simple statistics. The statistics include the mean and estimated bias of the quality control samples, and the relative random standard deviation (RRSD) and the systematic standard deviation (RRSD/$\sqrt{n}$). Finally, the established population standard deviation and Z-score (= $\sqrt{n}$ xBIAS/POP SD) are printed. The z-score is the usual value plotted on a Shewhart control chart. We suspect that a bias exists if the magnitude of the z-score is large ($\geq$3).

QC RESULTS

#	DENSITY
1	1.681646
2	1.681657
3	1.681632

MEAN	=	1.6816451
BIAS	=	0.2816E-5
RSSD	=	1.2855E-5
SYS SD	=	7.4218E-6
POP SD	=	1.2600E-5
Z	=	0.2235

FIGURE 4. Measurement Control Example

ANALYSIS OF PRODUCTION SAMPLES

The purpose of this portion of the algorithm is to identify sampling/mixing problems. This is accomplished through a statistical and graphical analysis of the density data. Additionally, duplicate analyses are used to check the quality of analytical work. Problem analytical results can be identified and the analysis can be rerun without suspect data.

This algorithm can accommodate two trailers. In practice six samples are drawn systematically from the tank output as the uranyl nitrate solution is transferred into each trailer. Two aliquots from each sample are analyzed for density. The aliquots are divided into two groups, each group containing one of the aliquots. Then the aliquots are arranged in a randomized sequence within the first group as shown in Figure 5. This sequence is reversed for the second group. The sampling and analysis of samples is performed in the same way on the second trailer.

Trailer 1

1 2 3 4 5 6
Sample Order

QC 6 2 5 4 1 3 QC 3 1 4 5 2 6 QC
Measurement Order

FIGURE 5. Top: Samples are drawn and numbered consecutively. Bottom: The order of measurement is randomized. Numbers refer to the sample from which the aliquot was derived; "QC" refers to quality control or calibration samples.

Results are analyzed both analytically and graphically. An analysis of variance is performed on each trailer to determine if the sample densities significantly differ. A test is performed to pool variances due to analysis. Figure 6 depicts the structure of the analysis of variance table in the usual situation when block differences are insignificant.

ANOVA

Source	Degrees of Freedom	F-Ratio
Trailer 1 Samples	5	MS(Tr.1 Samples)/MS (Analysis)
Trailer 2 Samples	5	MS(Tr.2 Samples)/MS (Analysis)
Analysis (Pooled Residuals Including Block Effect)	12	

FIGURE 6. Analysis of Variance.

In this situation the effect due to samples is tested in the usual fashion as the F ratio of the samples mean square to the pooled analysis mean square. If the result is significantly large then there is sample-to-sample variation. We believe that the solution entering the trailer is not well-mixed or a sampling problem has occurred. The relative random standard deviation due to analyses is ($\sqrt{MS(Analyses)}$/Mean Density)x100%. However, if the result is insignificant, then there is no sample-to-sample variation. In this case it appears that the transferred solution is well-mixed and the relative random standard deviation is ($\sqrt{MS(Total)}$/Mean Density)x100%, where $\sqrt{MS(Total)}$ is the standard deviation of all measurements.

The estimated density for each trailer is the mean of all analyses on that trailer. A limit of error is also placed on the mean density for each trailer, based on the results on the analysis of variance.

Graphs of the results are also used to investigate sampling/mixing problems. Two graphs are routinely printed on the narrow 24 column printed output. The first graph plots the standardized mean of each sample against the sampling order. The standardized mean is simply the number of standard deviations which the sample mean lies above the overall trailer mean (if negative, then the sample mean lies below the overall trailer mean). An example is given in Figure 7. The mean density of each sample is printed in the left margin. The numbers on the horizontal axis indicate the number of standard deviations that the sample mean lies above or below the trailer mean. The numbers on the graph represent the sample number; the symbol "<" indicates that sample 1 from trailer #0XX was at least three standard deviations below the mean.

```
PLOT OF SAMPLE MEANS
   SHIPMENT  #0XX
SD'S    -3-2-1 0 1 2 3
DENSITY -+-+-+-+-+-+-+-
1.010013<       +
1.010299        +  2
1.010311        +    3
1.010311        +    4
1.010306        +   5
1.010315        +    6
```

```
PLOT OF SAMPLE MEANS

   SHIPMENT  #0YY
SD'S    -3-2-1 0 1 2 3
DENSITY -+-+-+-+-+-+-+-
1.009098        1
1.009106        2
1.009098        3
1.009098        4
1.009101        5
1.009130        + 6
```

FIGURE 7. Plot of Standardized Sample Means.

The second graph is a diagnostic aide in identifying problem analyses. Standard deviations are calculated separately for the two measurements on each sample. Clearly, these values will be large if the duplicate measurements are not in good agreement. These values are standardized and plotted against the order of measurements. The largest of these standardized values is a Grubb's-type statistic for testing for an outlier. Refer to Figure 8. One can observe that none of the statistics appeared large. Therefore, it appears that none of the analyses is suspect.

```
PLOT OF STATISTICS
FOR ANALYSES

SHIPMENT  #0XX

SD'S        0  1   2   3
RATIO      +---+---+---+
 1.10       +   6
 0.21       2
 1.76       +       5
 1.34       +    4
 1.56       +     1
 1.64       +     3
 Grubb's Statistics = 1.76
   No Outliers Detected
```



```
PLOT OF STATISTICS
FOR ANALYSES

SHIPMENT  #0YY

SD'S       0   1   2   3
RATIO     +---+---+---+--
 2.32      +         3
 1.79      +       1
 0.56      + 4
 0.64      + 5
 1.07      +   2
 1.01      +   6
 Grubb's Statistics = 2.32
   No Outliers Detected
```

FIGURE 8. Plot of Standardized Sample Means.

The program calculates a Grubb's-type[2] statistic. If its value is significantly large, then outliers are identified at the bottom of the graph. If its value is insignificant, then the message "no outliers detected" is printed at the bottom of the graph. If the user discovers outliers that should be eliminated, then the software permits the user to suppress them, and redo the analysis without them.

SUMMARY

The density meter algorithm is automatic, flexible, compact, and easy to maintain. The menus simplify the entry of operator information. The measurement control program produces a high degree of confidence in the density measurements. The algorithm is successful in detecting sampling/mixing problems.

REFERENCES

[1]N.R.Draper and H.Smith, Applied Regression Analysis, John Wiley and Sons, Inc., New York, 1981

[2]John L.Jaech, Statistical Methods in Nuclear Material Control, Technical Information Center, United States Atomic Energy Commission, 1973