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FINAL REPORT

TRACER TECHNIQUE FOR URINE VOLUME DETERMINATION AND
URINE COLLECTION AND SAMPLING BACK-UP SYSTEM

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URINE VOLUME DETERMINATION STUDY

1.0

INTRODUCTION

This study was initiated to further investigate the feasibility, functionality and overall accuracy of the use of lithium as a chemical tracer in urine, thereby providing a means for indirect determination of total urine volume by atomic absorption spectrophotometry method. Experiments were conducted to investigate the parameters of instrumentation, tracer concentration, mixing times, and methods for incorporating the tracer material in the urine collection bag, and to refine and optimize the urine tracer technique to comply with Skylab schema and operational parameters of $\pm 2\%$ of volume error and $\pm 1\%$ accuracy of amount of tracer added to each container. In addition, a back-up method for urine collection and sampling system was developed and evaluated. This back-up method incorporates the tracer technique for volume determination in event of failure of the primary urine collection and preservation system. One chemical preservative was selected and evaluated as contingency chemical preservative for the storage of urine in event of failure of urine cooling system.

2.0

PHASE I

2.1

Purpose:

This phase evaluated techniques for the improvement of the accuracy of the tracer method. This phase also determined optimum tracer concentration and mixing time. Consideration was given to possible use of multi tracers, solvents as diluents for analysis and techniques for reducing instrument scatter and error.

2.2 Task a

2.2.1 Description of Task

Determine spectrophotometer scatter and error with concentration of lithium tracer in urine of 1, 2, 5, 10, 20, 30 and 50 ppm.

2.2.2 Method

Tracer analyses were conducted with Perkin Elmer Model 403 Atomic Absorption Spectrophotometer with air-acetylene fuel mixture system. The instrument was prepared and peaked for optimum element detection in the same manner each time to maintain best performance and reduce scatter and error. The detection limit of the spectrophotometer is 0.5 to 5 $\mu\text{g/ml}$. Instrument sensitivity is considered at 0.03 $\mu\text{g/ml}$ lithium and linear up to concentrations of approximately 2 $\mu\text{g/ml}$ in aqueous solution. Aqueous lithium tracer was delivered volumetrically in all cases and dilutions were prepared in volumetric glassware with deionized water. All samples withdrawn for analysis were done with volumetric pipettes. Although there are several variables that may introduce errors in analysis, most of the potential variables were checked in the laboratory against suitable standards. Tracer salt purity was checked against standard analytical solutions of lithium from Harleco Company used to calibrate the spectrophotometer.

Experiments were conducted with urine diluted (1:10) with water and urine containing tracer at various concentrations to investigate instrument scatter and error and to improve accuracy of lithium tracer determination by atomic absorption. The test samples were aspirated at several different rates to evaluate the stability of the nebulizer and efficiency of the sample tube to deliver a constant flow of solution to the burner and remain free from clogging. It was noted that

2.2.2 (continued)

tube clogging could be eliminated by using diluted urine. Instrument response was improved and scatter was reduced by maintaining a constant rate of aspiration. An aspiration rate of 6 to 8 ml per minute was found satisfactory and used for all subsequent analysis. Lithium concentrations of 1 to 2 ppm in urine diluted (1:10) showed the least instrument scatter, and percent error was reduced. Precision of instrument was also greatly improved by the use of dilute aqueous test sample.

2.2.3 Results

The amount of tracer is primarily determined by the accuracy and detection limits of the instrument. The highest level of accuracy was seen of lithium concentration in 1 to 2 ppm range prepared for atomic absorption analysis. When aspiration rate of diluted urine is maintained constant, instrument scatter and level of error was definitely improved.

2.2.4 Conclusion

The conclusion is that lithium concentration in diluted urine should be in 1 to 2 ppm range to maintain high level accuracy and precision.

The findings also suggest that the tracer concentration in the urine collection bag should be at least 30 mg lithium when maximum urine volume of 3,000 ml is considered, or an average of 10 mg lithium per liter of urine. Therefore, one ml available for analysis, diluted 1:10, will contain 1 ppm Li.

2.3 Task b

2.3.1 Description of Task

Determine effect of mixing time of 1, 2, 5, 10 and 30 minutes on analytical scatter and error, at lithium or other tracer concentrations of 1, 2, 5, 10, 30 and 50 ppm. A standardized method of mixing shall be developed and

2.3.1

(continued)

utilized for these experiments. The effects of a urine temperature at 36° F in mixing will be determined.

2.3.2

Method

Lithium chloride stock solution (1,000 ppm Li) was prepared in the laboratory with deionized water. Lithium standard from Harleco was used to calibrate the spectrophotometer. The experiments were prepared by delivering 5 ml of 1,000 ppm Li and adding 495 ml of pooled chilled urine (36° to 40° F) in volumetric flasks. The chilled contents were mixed for 1, 2, 5, 10 and 30 minutes, withdrawing an aliquot of urine for analysis after each mixing time. Mixing was accomplished by inverting the vessel approximately 30 times per minute.

Ten mls of the urine-lithium contents were diluted with deionized water and 10 ml of potassium chloride solution (10,000 ppm KCL) in 100 ml volumetric flasks. This placed the lithium concentration of dilute urine (1:10) at 1 to 2 ppm.

The potassium chloride solution was used as a buffer agent to help reduce scatter and interference.

The tests were conducted by inserting the sample tube from the spectrophotometer directly into the contents of the flask and aspirated at a constant rate of approximately 6 to 8 ml per minute. The concentrations shown in all experiments in this report were the average of 100 samplings, obtainable with this model spectrophotometer. Standard solutions were prepared by diluting lithium nitrate (1,000 ppm Li) spectrographic standard with water and potassium chloride solution, the same as in all test samples. This offered a direct comparison of the test samples with a reliable standard.

2.3.3

Results

The results of this experiment (Table 2.3.3.A and Table 2.3.3.B) show that a complete dispersion of lithium tracer in chilled urine can be attained by proper mixing.

TABLE 2.3.3.AMixing Time-Mixing Method vs. Accuracy

<u>Mixing Time</u>	<u>Li Std. 1 ppm conc.</u>	<u>Li 1 ppm Conc. Urine Diluted 1:10</u>	<u>Li Conc. By Analysis</u>	<u>Percent Error</u>
1 Minute	1.00	1.00	1.00	0%
2 Minutes	1.00	1.00	1.01	1%
5 Minutes	1.00	1.00	1.02	2%
10 Minutes	1.00	1.00	1.02	2%
30 Minutes	1.00	1.00	1.01	1%

TABLE 2.3.3.BMixing Time-Mixing Method vs. Accuracy

<u>Mixing Time</u>	<u>Li Std. 2 ppm conc.</u>	<u>Li 2 ppm Conc. Urine Diluted 1:10</u>	<u>Li Conc. By Analysis</u>	<u>Percent Error</u>
1 Minute	2.00	2.00	2.01	0.5%
2 Minutes	2.00	2.00	2.04	2%
5 Minutes	2.00	2.00	2.03	1.5%
10 Minutes	2.00	2.00	2.02	1%
30 Minutes	2.00	2.00	2.01	0.5%

2.3.4

Conclusion

A homogeneous mixture is evident in the first or second minute of mixing. The findings suggest that at least one (1) full minute is necessary to attain optimum dispersion of lithium tracer in pooled chilled urine.

2.3.5 Prototype Urine Collection Bags

Experiments were prepared as in 2.3.2 except that 5 mls of lithium (1,000 ppm Li) were delivered into the prototype bag through the orifice provided. Four-hundred ninety-five (495) mls of pooled chilled urine were delivered volumetrically, and the contents were mixed for one (1) full minute. The mixing was done manually by closing the orifice and holding the bag horizontally between the hands. With a slight lateral movement of the hands and arms the contents were sloshed from side to side in the bag. Although some foaming of the chilled urine was evident, there was no indication of interference with dispersion of tracer nor at time of sample extraction for analysis.

Mechanical methods for mixing are available; however, mixing manually proved satisfactory. Urine test samples were withdrawn soon after the mixing stopped and diluted as in 2.3.2.

2.3.6 Results

The results of this experiment (Table 2.3.6A) show that a good dispersion of lithium in urine in prototype urine collection bags can be attained by manually mixing the contents for one (1) full minute.

See Table 2.3.6A on next page.

2.3.6 (continued)

TABLE 2.3.6A

Mixing Time-Mixing Method vs. Accuracy

<u>Mixing Time (Minutes)</u>	<u>Urine Volume</u>	<u>Li Std. 1 ppm Conc.</u>	<u>Li Conc Dilute Urine (1:10) ppm</u>	<u>Li Conc. By Analysis ppm</u>	<u>Percent Error</u>
1	495	1.00	1.00	1.00	0%
1	495	1.00	1.00	1.00	0%
1	495	1.00	1.00	0.99	-1.0%
1	495	1.00	1.00	1.00	0%
1	495	1.00	1.00	0.99	-1.0%
1	495	1.00	1.00	1.00	0%
1	495	1.00	1.00	0.99	-1.0%
1	495	1.00	1.00	1.00	0%
1	495	1.00	1.00	0.99	-1.0%
1	495	1.00	1.00	1.00	0
1	495	1.00	1.00	0.99	-1.0%
1	495	1.00	1.00	1.00	0%

2.3.7 Conclusion

In order to obtain a satisfactory dispersion of lithium in pooled chilled urine, the contents should be mixed for one (1) full minute. The mixing can be readily accomplished by the manual method stated in 2.3.5. The results in Table 2.3.6.A are consistent and within the allowable volume error.

2.4 Task c

2.4.1 Description of Task

Determine the effects of the use of acetone, methanol, and ethanol as diluents for the analysis of tracer in urine, using the tracer concentration and mixing time which shows the minimum scatter and error as determined in Task a and Task b.

2.4.2 Method

Tests were conducted to establish the use of organic solvents as diluents for tracer analysis and also reduce instrument background interference.

Aqueous test solutions were prepared from each of the solvents in 2.4.1 and aspirated at constant rate.

In every case the dilute solvents caused considerable flame effects and interference. The level of scatter and error that was experienced was higher than the limits allowable. The use of solvents may also constitute a potential safety hazard when mixed with the burner gases and ignited.

2.4.3 Results

The use of organic solvents as diluent for lithium analysis contributed a high degree of interference and instrument scatter and was definitely no improvement over deionized water as the diluent.

2.4.4 Conclusion

Organic solvents as diluents for lithium tracer were considered unacceptable because of the high interference contributed.

The use of deionized water is by far superior to solvents.

2.5 Task d

2.5.1 Description of Task

Determine the effects of the use of chromium and lithium-chromium tracer on analytical scatter and error, using tracer concentration and mixing time as determined in Task a and Task b.

2.5.2 Method

Tests of a qualitative nature were conducted to determine the possible use of chromium and lithium-chromium tracer for urine volume determination. Since the level of error found in chromium urine tests was higher than that allowed, the tests with chromium-lithium showed considerable increase in error as a multi-tracer method. It was also learned that a complete change-over of instrument adjustments and mechanics to analyze both tracers was necessary in the multi-tracer scheme, therefore creating a greater instrument error.

2.5.3 Results

The results of these tests indicated that the use of chromium tracer, alone or in combination, would incur a percent error greater than $\pm 2\%$.

2.5.4 Conclusion

The use of this tracer scheme is not acceptable because of error magnification.

2.6 Task e

2.6.1 Description of Task

Investigate possibilities for reducing scatter and error caused by the analytical procedure and instrumentation. Examine optical filters, instrument pick-up tube depth in solution, pick-up tube length, and flame effects.

2.6.2 Method

2.6.2.1 Optical Filters

Optical filters for the spectrophotometer were examined to determine if scatter and error could be reduced through the use of a single or multi-filter system. The examination ruled out the external mounting of filter to improve instrument procedure. However, it was learned that the use of internal filter system incorporated in this model considerably improved instrument performance.

2.6.2.2 Burner

The proper alignment of the four-inch single slot burner also increased the performance. This consisted of horizontal positioning of the burner in line with the light path in the combustion chamber of the spectrophotometer.

2.6.2.3 Flame effect

Best performance was also experienced with an even oxidizing flame of average height.

2.6.2.4 Potassium Chloride Solution

A solution of potassium chloride (10,000 ppm KCL) was prepared by dissolving 18.5 gm potassium chloride crystals in a liter of water. The ten ml. volume used in diluting the urine (1:10) in a 100 ml flask acted as a buffer agent and generally improved the analytical procedure. This solution was used in preparing the test and reference standard solutions for analysis.

2.6.2.5 Instrument Pick-Up Tube

Tests were made with the instrument sampling tube at different depths in the test solution. Depths of 1/4-inch, 1/2-inch, 1-inch and 2-inches from the surface were investigated. The depth of sampling tube in solution showed no significant evidence of influencing the analysis. However, it should be pointed out that the length of sampling tube does change the rate of aspiration, and it is suggested that operating aspiration rates be established with each tube size used. A 7-inch long polyethylene tubing that would fit securely over the nebulizer stem was used successfully for these tests. An aspiration rate of 6 to 8 mls per minute proved satisfactory with this tube, and has since been used in analytical procedures.

2.6.2.6 Volumetric glassware

In all procedures applicable to the tracer technique, volumetric glassware was employed. The glassware was nitric acid washed and properly rinsed before use. Precision, quality Class A, serialized, volumetric pipettes purchased from Fisher Scientific Company were used to maintain the required level of accuracy, $\pm 1\%$ of amount of tracer added to each container. Proper analytical and quantitative procedures were employed at all times.

2.6.2.7 Lithium Stock Solution (6,000 ppm Li)

The lithium stock solution was prepared in the laboratory from Lithium Chloride, powder, Fisher Scientific certified. The powder was oven dried overnight, and 36.5856 gms of LiCl were carefully weighed and diluted in a liter of deionized water. Therefore, one ml stock solution contained 6,000 ppm or 6 mgs Li. It should be pointed out that a standard prepared from the same stock solution used for the urine collection bags will satisfactorily fill the standard role and further reduces tracer error.

2.6.2.8 Spectrographic Lithium Standard

The experiments conducted in the entire study for this contract were directly compared against a reliable spectrographic standard of Lithium Nitrate (1,000 ppm), diluted to the desired concentrations with water and potassium chloride, same as in tests in 2.3.2. The standard is a product of Harleco Company.

2.6.2.9 Urine Standard

A urine standard was not considered for these experiments because of potential variables that may exist. However, a synthetic urine standard could probably be used as reference standard, but no synthetic urine standard was used in this study.

2.6.2.10 Results

The findings of Task e suggest that employing proper analytical procedure and good control over the mechanics of instrumentation, scatter and error are reduced.

2.6.2.11 Conclusion

Scatter and error are reduced by using proper procedure and control and by preparing standard to calibrate instrument from same lithium stock solution used in collection containers.

2.7 Task f

2.7.1 Description of Task

Conduct these tests in such a manner that mass balance computation can be made in order to determine total recoverability of tracer.

This technique will enable a continuing evaluation to be made as to possible loss of tracer through sorption processes.

2.7.2 Method

2.7.2.1 Sorption Study using UCMSS Prototype Bag and Filter Material

The prototype Teflon bags were manufactured by Dilectrix Corporation, and a representative sample of the filter material used in bag scheme was supplied separately.

The tests were prepared by delivering 5 ml of stock lithium solution (2.6.2.7) to each bag volumetrically through the bag orifice. Three-inch squares of the filter material were placed in glass containers, and 5-ml of stock solution were delivered to each vessel. The bags and the glass containers were oven dried overnight at approximately 110° F with circulating air stream. Six-hundred (600) mls of pooled chilled urine (36° to 40° F) were added to each container and mixed for one minute.

Samples were extracted for analysis and diluted (1:50). The Sorption Study was prepared starting with Week 0 through Week 5. During the interim between weeks, the test bags and container were kept refrigerated at approximately 36° F. At the end of each week the contents were mixed again for one minute, and samples were extracted for analysis.

2.7.2.1 (continued)

TABLE 2.7.2.1.A

UCSS PROTOTYPE BAG SORPTION STUDY

Week	Bag 1			Bag 2			Bag 3		
	A	B	C	A	B	C	A	B	C
0	1.00	0.99	1.00	0.99	0.99	0.99	0.99	0.99	0.99
1	1.00	1.00	1.00	1.01	1.01	1.01	1.00	1.00	1.00
2	0.99	1.00	0.99	1.00	1.00	1.01	1.00	1.00	0.99
3	0.99	0.99	0.99	0.99	1.00	1.00	1.00	1.00	1.00
4	1.00	1.00	1.01	0.99	0.99	0.99	1.01	1.01	1.01
5	1.01	1.01	1.01	1.00	1.00	1.00	1.01	1.00	1.00

TABLE 2.7.2.1.B

UCSS PROTOTYPE HYDROPHOBIC FILTER MATERIAL SORPTION STUDY

Week	Container 1			Container 2			Container 3		
	A	B	C	A	B	C	A	B	C
0	0.99	0.99	0.99	1.01	0.99	0.99	1.00	0.99	1.00
1	1.01	1.00	1.00	1.01	1.01	1.00	1.00	0.99	1.00
2	1.00	1.01	1.00	1.01	1.01	1.00	1.00	0.99	1.00
3	1.01	1.02	1.02	1.00	1.00	1.00	1.00	0.99	0.99
4	1.00	0.99	1.00	1.01	1.00	1.00	1.00	1.00	1.00
5	1.00	1.00	1.01	1.01	1.02	1.01	1.00	1.00	0.99

Conditions:

Lithium conc. in each container - 30 ngs

Diluted urine for analysis - 1:50

Lithium standard - 1 ppm

Readings are in ppm