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AUTOMATED ANALYSIS OF LITHIUM SOLUTIONS

R. H. Gaddy

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Savannah River Laboratory

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AUTOMATED ANALYSIS OF LITHIUM SOLUTIONS

by

Rufus H. Gaddy

Approved by

E. L. Albenesius, Research Manager
Analytical Chemistry Division

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E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA

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ABSTRACT

An automated flame photometric method was developed for the precise determination of lithium in highly radioactive process solutions containing curium, americium, and fission product radionuclides.

CONTENTS

LIST OF TABLES AND FIGURES

AUTOMATED ANALYSIS OF LITHIUM SOLUTIONS

INTRODUCTION

In the recovery of americium and curium in the Tramex separations process, these elements are extracted from an 11M lithium chloride solution into a mixture of tertiary amine chlorides in diethylbenzene. Because the extraction of americium and curium is strongly dependent on the lithium concentration, an analytical method was required for determining lithium with a high degree of accuracy and precision.

The high radiation level of the Tramex process feed solution is a primary consideration in the analytical methods to be considered. Chemical methods(1,2) are, in general, not specific for lithium, are long and tedious, and require large samples for weighing lithium as lithium sulfate. These disadvantages of the chemical determination of lithium in a highly radioactive solution prompted the search for an instrumental method. The polarographic determination(3) of the alkali metals with tetraethylammonium hydroxide as the supporting electrolyte is not precise enough to meet the specifications in the Tramex process.

Conventional flame photometric equipment has been used to measure the lithium concentration of samples that were separated from radioactive lanthanides and actinides by passage through a calcium fluoride column.(4) Under ideal conditions, a relative standard deviation of 2% was attained, but in routine analysis the precision was less, and adequate control of the process was difficult. Although flame photometric methods are claimed to be precise to only 2-3%, it appeared feasible to develop an automated flame photometric method for determining lithium with a higher degree of precision.

SUMMARY

A flame photometer attachment was adapted for use with the "AutoAnalyzer"* to provide an automated analytical method for the routine determination of lithium in Tramex process solutions. This method has been used successfully in the course of the development of the Tramex process at the Savannah River Laboratory.

Radioactive lanthanides and actinides are removed from the Tramex solution by passing the sample through a calcium fluoride column before analysis. The purified solution is fed through the "AutoAnalyzer" where

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*Trademark of Technicon Controls, Inc., Chauncey, N. Y.

it is mixed with a potassium internal standard, and is then fed to the burner of the photometer. Light from the flame is passed through interference filters and the ratio of the intensity of the lithium line to that of the potassium line is recorded.

The relative standard deviation for the analysis of Tramex feed solutions is ±1.4%. The combined noise level and drift of the instrument system represents only ±0.2% error.

DISCUSSION

EQUIPMENT

The equipment consisted of a calcium fluoride column, an "AutoAnalyzer" proportioning pump and automatic sampler, and a flame photometer attachment for the "AutoAnalyzer." The preparation of the calcium fluoride column(5) (shown in Figure 1) and the operation of the proportioning pump(6) and automatic sampler(7) have been described.

The flame photometer(7) attachment shown in Figure 2 was designed for the determination of sodium and potassium in blood serum with lithium used as an internal standard. Since the photometer was designed for the output signal to be proportional to the ratio

$$\frac{\text{sodium or potassium concentration}}{\text{lithium concentration}},$$

the interference filters were rearranged in their semipermanent positions to give an output signal that was directly proportional to the lithium concentration.

The unusual features of the flame photometer are a uniquely designed burner and a built-in range expander. The range expander provides a threefold expansion of the recorder scale. The burner is shown in Figure 3. Propane and oxygen, each at 10 psig, are mixed in a metal chamber prior to entering the burner. The main flame gases issue through the annulus surrounding the sample capillary at speeds adequate for atomization of the liquid sample stream. The auxiliary flame burns at the tips of the three capillaries located symmetrically at the periphery of the burner and stabilizes the main flame. For accurate control of gas flow rates and flame conditions, both oxygen and propane are metered individually for each flame. The emitted light of interest, Li 670.8 mμ and K 766.5 mμ, is selectively isolated by interference filters and detected with cadmium sulfide photocells. The ratio of the signals from the photocells activates a strip chart recorder. The absence of drift and the low noise level of this automated method for a steady state condition are shown in Figure 4. The noise level represents an error of ±0.2% in the method.

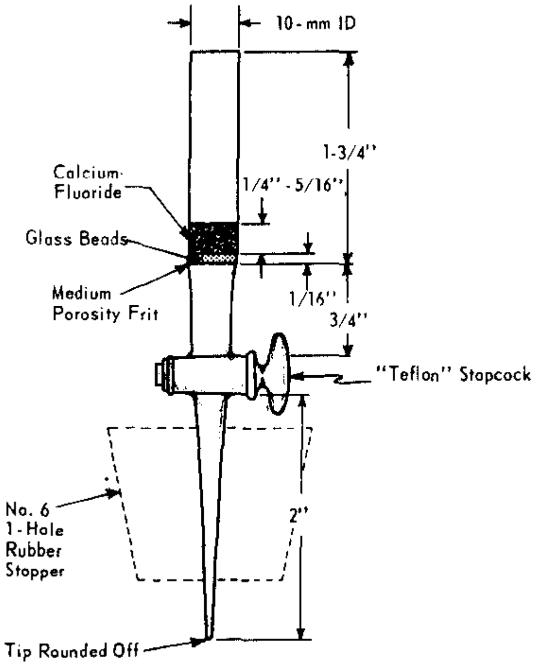

FIG. 1 CALCIUM FLUORIDE COLUMN

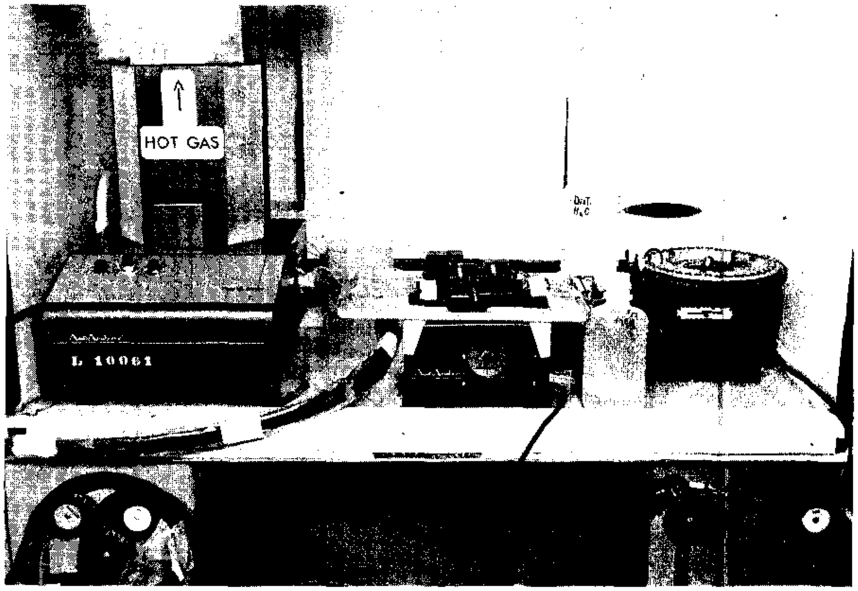

FIG. 2 FLAME PHOTOMETER ATTACHMENT WITH PROPORTIONING PUMP AND AUTOMATIC SAMPLER

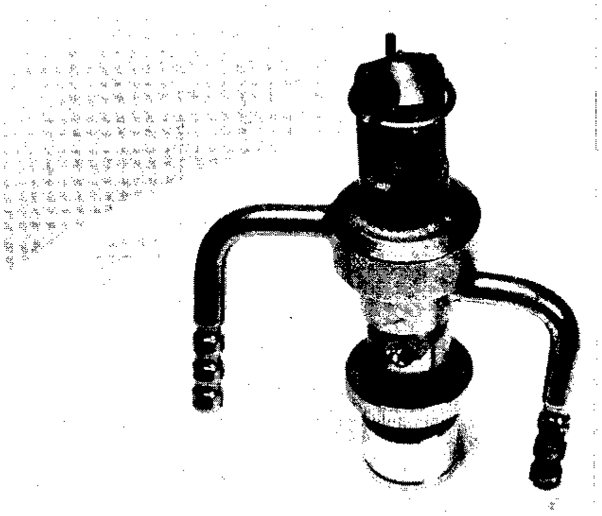

FIG. 3 FLAME PHOTOMETER BURNER

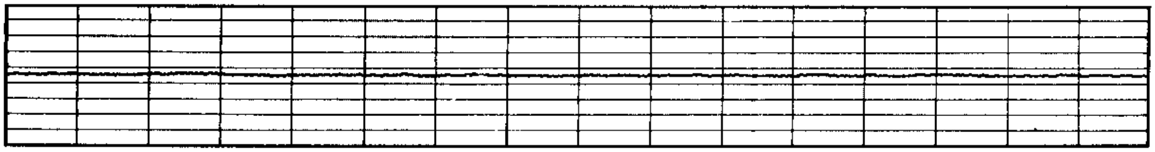

FIG. 4 RECORDER TRACE OF NOISE LEVEL DURING TIME REQUIRED FOR ANALYSIS OF SAMPLE AND STANDARDS

STANDARDIZATION

Powdered lithium chloride (Allied Chemical Co., Reagent Grade) was dried at 110°C for 24 hours. Calcium, barium, lead, tin, and iron, each at less than 0.01 wt %, were detected in the powder by spectrographic analysis. These analyses confirmed the manufacturer's assay of 98.0 wt % LiCl.

Standard solutions of 8 to 12.5M LiCl were prepared from the dried powder. These solutions were diluted 1000-fold and adjusted to 0.05M HNO_3 and 0.03 g La/l. The lanthanum is used as a stand-in for rare earths in the Tramex feed solutions.

Figure 5 shows a calibration curve prepared with the diluted standards.

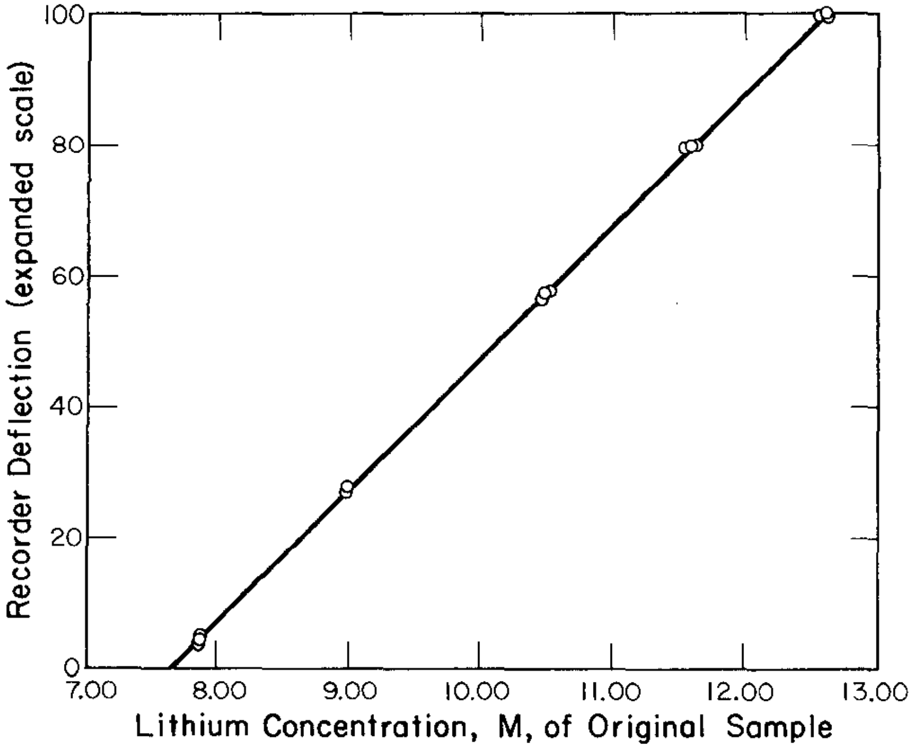

FIG. 5 LITHIUM CALIBRATION CURVE

PROCEDURE

Tramex process samples and standards that bracket the estimated value of each sample are run in duplicate by the following procedure: Samples containing about 1 g ^{244}Cm/l and 11.0M LiCl are diluted manually 1000-fold with 0.05M HNO_3. The alpha activity of diluted samples is approximately 10^8 dis/(min)(ml). A 0.500-ml aliquot of the dilution is made slightly alkaline with concentrated ammonium hydroxide and is carefully transferred to a calcium fluoride column. After the flow through the column is regulated to about 0.2 ml/min, the sample is washed through the column with 0.1M ammonium hydroxide—0.005M ammonium nitrate solution. The sample and washes are collected in a 10-ml volumetric flask and are quantitatively diluted with the wash solution. The calcium fluoride column decontaminates the sample by a factor of 5×10^6 by removing actinides and lanthanides. The decontaminated sample is transferred to three polystyrene cups, which are placed on the automatic sampler. The proportioning pump mixes the internal standard, 10^{-5}M KCl, with each sample and pumps the adjusted sample to the flame photometer at the rate of 40 sample cups per hour. The pumping manifold is shown in Figure 6.

Since the light emitted by lithium is proportional to the lithium concentration, and the photocells have a linear response to the emitted light, the recorder stylus deflection is proportional to the lithium concentration in the sample. A recorder chart tracing for a Tramex feed sample and standards is shown in Figure 7.

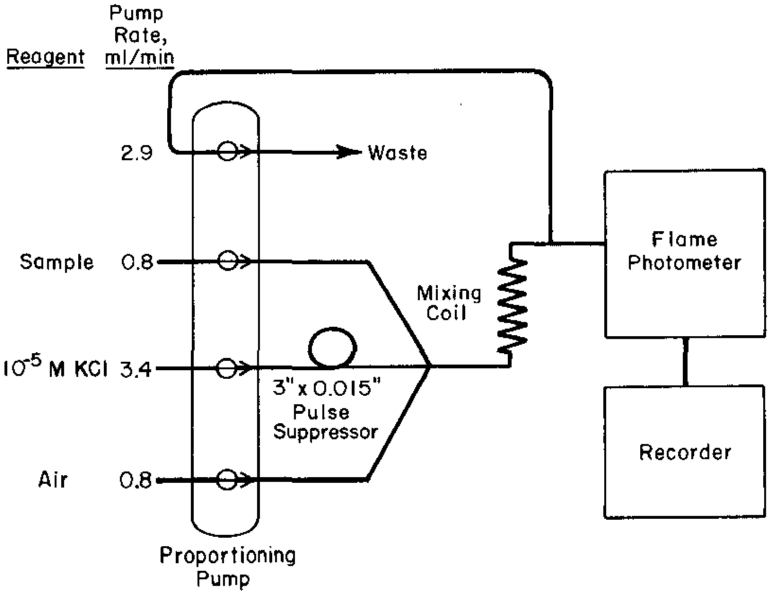

FIG. 6 FLOW DIAGRAM FOR AUTOMATED LITHIUM METHOD

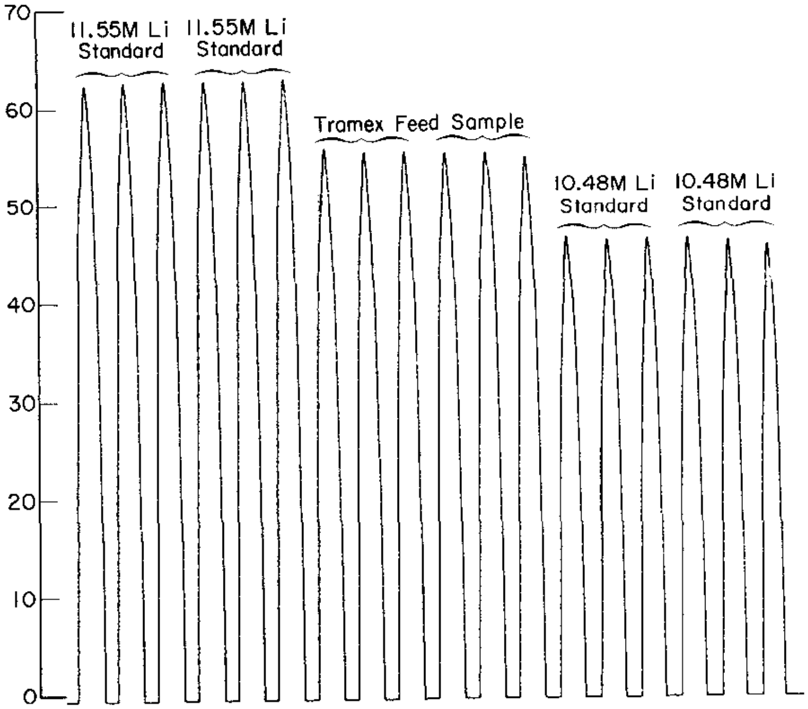

FIG. 7 RECORDER CHART SHOWING RATIOS OF INTENSITIES OF Li 670.8 mμ LINES TO K 766.5 mμ LINES FOR STANDARDS AND SAMPLE

PRECISION

The automated flame photometric method has been used successfully during the past eighteen months for obtaining precise lithium analyses on radioactive Tramex feed solutions as well as on nonradioactive samples from various scrub and reductant streams. The precision of the analysis was adequate for process control and is summarized in Table I.

TABLE I

Precision of Automated Flame Photometric Lithium Method

	Relative Standard Deviation, %
Instrument noise level	±0.2
Inactive lithium solutions	±0.4
Tramex feed solutions	±1.4

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