Determination of Potassium in Food Using the Technicon AutoAnalyzer Flame Photometer and Solid Prep Sampler

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A completely automated method has been developed for the determination of potassium in food using the Technicon AutoAnalyzer flame photometer and the Solid Prep sampler. Solid samples may be analyzed at the rate of 20 per hour. Potassium is completely extracted in 1 minute and 20 seconds by warm (50° C.) 0.5N ammonium acetate. The stirrer in the homogenizer has been modified to facilitate complete extraction within this time limit. The results are comparable with those obtained by conventional methods requiring ashing or manual extraction of potassium prior to flame photometric determination. Precision of this method for the analysis of potassium in tea is given by the result, 1.51 ± 0.03%. The procedure is applicable to other plant matter or materials containing soluble potassium salts, once the operating parameters have been established.

Potassium in a solution can be determined automatically by use of the Technicon AutoAnalyzer which consists of a liquid sampler, peristaltic pump, dialyzer, and flame photometer (3). Until now, however, there has been no automated system for the extraction of potassium from a solid sample with subsequent pumping of the sample through the analysis modules for the flame determination of extracted potassium. Potassium may be extracted from plant and organic matter by use of aqueous solutions of acid and ammonium acetate (1, 2) with proper agitation. It was felt that by use of the Technicon Solid Prep sampler, solid samples could be extracted sequentially in the homogenizer, using the proper extracting solution. An automated method is given for the extraction of potassium from organic matter with subsequent automated flame analysis.

Experimental

Reagents. All reagents used were analytical grade. The following standard solutions were prepared: LiNO₃, 1000 meq. per liter in 2N H₂SO₄; LiNO₃, 125 meq. per liter in 0.25N H₂SO₄; KCl, 10 mg. of K per ml. Other dilutions were made from the K stock standard.

Apparatus. The basic Technicon AutoAnalyzer is used in conjunction with the Solid Prep sampler. The homogenizer blades of the sampler were modified (Figure 1) to effect more efficient extraction. Two control gears are available to determine the operating cycle of the sampler. A 10-minute gear allows the sample to homogenize for approximately 4 minutes and treats only six samples per hour. A 3-minute gear allows the sample to homogenize for approximately 1 min-

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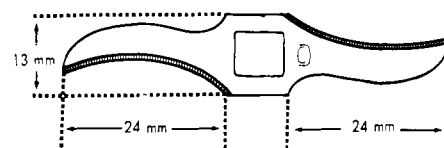[2] Present address, Tect, Inc., Northvale, N.J.

Figure 1. Modified homogenizer blade

ute and 20 seconds and treats 20 samples per hour. The 3-minute gear was the only practical gear to utilize, if the Solid Prep unit was to be efficient, timewise. To supply the 0.5N NH₄C₂H₃O₂ extraction solvent, a 10-liter bell jar was equipped with a heating element, thermoregulator, and stirrer. The 0.5N NH₄C₂H₃O₂ was maintained at 60° to 65° C., and the attendant heat losses during transit to the homogenizer resulted in a final temperature of about 50° C.

The sampler cups were filled as follows: The first five cups contained 10 ml. of standard solutions of KCl at various concentrations (diluent delivery control at 90 ml.) to obtain a calibration curve, while 1 gram of the ground samples was placed in the remainder of the cups (diluent delivery control at 100 ml.). It is advisable to include at least one standard sample for each 20 sample analyses to establish stability of the operation. The schematic drawing of the basic analytical methodology is given in Figure 2. The tubing size may be varied depending on the sample and concentration of potassium.

Standardization of Instrument. Follow the instructions given (4) for lighting, warm-up, and adjustment of flame photometer prior to analysis. After adjusting the flame, connect the sampler to the manifold system and the sample line from the dialyzer to the flame housing. Set the diluent delivery control of sampler to deliver 90 ml. Turn the programmer switch "on" and allow the sampler to complete three cycles in order to equilibrate the temperature inside the homogenizer vessel. Pipet into the sampler cup 10 ml. of the most concentrated standard solution that will be used to prepare the calibration curve. The concentration of
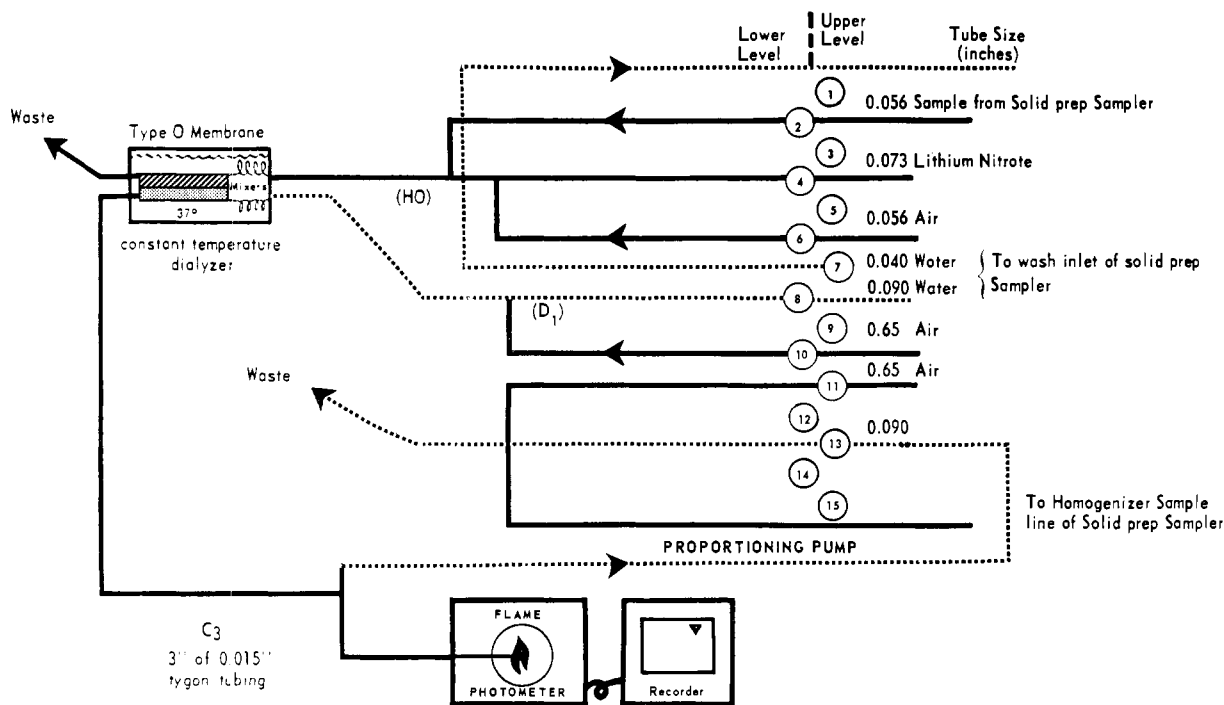
Figure 2. Schematic diagram for potassium determination using the Solid Prep sampler

this solution is 10 times the needed concentration but will be diluted by a factor of 10 in the homogenizer. Allow the standard to homogenize. Turn programmer control between 50 and 70 and programmer switch "off." Allow the solution to pass through the analytical train continuously. Adjust the recorder to read 95% transmittance. Continue the operation to obtain a base line. A stable base line should be obtained after 10 to 15 minutes. Prepare a calibration curve to include the desired concentration range using standard KCl solutions. The first five cups are used for these standards.

Sample Preparation and Extraction. Samples were ground in a double-bladed Brabender laboratory grinder to determine the effect of particle size on extraction time. Longer grinding gave smaller particle sizes. Finally, sample preparation, particularly of tea, consisted of grinding 30 grams of sample for 3 minutes. Some materials, however, required a longer grinding time to achieve a pulverized and completely homogeneous sample. A Waring Blendor approximating the homogenizer of the sampler was used in conjunction with several extraction media—such as solutions of HCl, H_2SO_4, CH_3COOH, $NH_4C_2H_3O_2$, and water—at several temperatures and various sample-to-solvent ratios to choose the extraction parameters and medium.

Results and Discussion

Extraction Parameters. Since $0.1N$ HCl had been used successfully to extract potassium from plant tissue (1), it was tried in this instance. Using this acid solvent and 1 gram of ground tea leaves, extraction efficiency as a function of residence time in the homog-

enizer of the sampler was studied. The recoveries of 71, 79, 85, and 87% for homogenization times of 1, 2, 3, and 5 minutes, respectively, ruled out the use of $0.1N$ HCl under these conditions, since a residence time of 1 minute and 20 seconds as the maximum allowable for a reasonable analysis rate of 20 samples per hour.

It seemed logical to investigate the extraction efficiency using other concentrations of HCl, other acids, and ammonium acetate (1). The results obtained using the Waring Blendor mentioned above utilizing 100 ml. of extractant, 1 gram of ground tea leaf, and 1 minute of extraction time, are reported in Table I. All of the extractants showed recoveries of 95 to 100% for some specific concentrations. However, other factors had to be considered. Depression of the flame was noted when high concentrations of H_2SO_4, HCl, CH_3COOH, and $NH_4C_2H_3O_2$ were used. When HNO_3 and CH_3COOH were used as extractants, the samples foamed excessively. The foaming tendency was reduced with Dow Antifoam spray, but this caused interference in the determination. Although H_2SO_4 completely extracted potassium, it was eliminated as an extractant because of the necessity for special tubing when used in the AutoAnalyzer system. Thus, considering all factors, HCl and $NH_4C_2H_3O_2$, of the six extractants examined, were most suitable for further study.

The extraction media $0.25N$ to $0.5N$ HCl and $0.5N$ $NH_4C_2H_3O_2$, which gave excellent results in the Waring Blendor (Table I), were employed with the sampler using a 1 minute and 20 seconds extraction time, and poor recoveries were obtained. The homogenizer blade was modified (Figure 1), and the extraction efficiencies of both blades were compared for five

Table I. Evaluation of Extractants Using a Waring Blendor

Extractants[a]	Normality[b]	% Recovery[c]
HNO₃	0.6	100
	0.9	97
	1.2	96
	1.6	98
	1.9	97
	3.1	98
HCl	0.25	100
	0.4	99
	0.5	100
	1.0	98
	1.4	94
	2.6	89
H₂SO₄	0.1	98
	0.4	101
	0.6	78
	3.6	78
CH₃COOH	0.4	79
	0.6	104
	3.0	79
NH₄C₂H₃O₂	0.1	81
	0.25	81
	0.5	100
	3.0	70

[a] One gram of tea leaf in 100 ml. of extractant at 25° C. for 1 minute extraction time.
[b] Concentration in homogenizer; however, diluted 1:10 before being passed through flame photometer.
[c] Control analyzed by extracting the potassium manually with HCl for 30 minute at 25° C.

tea leaf was mainly for the purpose of obtaining homogeneity in sampling and ease in handling in the Solid Prep sampler.

The effect of the ratio of sample weight to extractant volume was investigated. For 2.0, 1.4, 1.2, 1.0, 0.8, 0.6, and 0.5 gram of ground tea extracted with 100 ml. of $0.5N$ NH₄C₂H₃O₂ at 50° C., the recoveries were 100, 100, 100, 100, 93, 91, and 87%, respectively. There is no advantage of a sample-to-solvent ratio of less than 2 grams per 100 ml. Poor recoveries of samples smaller than 1 gram can be attributed to loss of particles on the side of the homogenizer.

Evaluation of Method. There are three major operational errors inherent to the analysis—sampling, sample preparation (Solid Prep), and analytical method. A series of experiments was conducted to analyze the significance of error contributed by each of these parameters.

An ashed tea sample was analyzed repeatedly for potassium using the AutoAnalyzer system (excluding the sampler). This gave the variation in the method. An average of 1.84% K was found with a standard deviation of 0.008 and a 95% confidence limit of 1.84 ± 0.02 (Table III).

A second experiment was carried out to determine the sampling error. A sample of tea was divided into five subsamples. The subsamples were ashed and each ash analyzed for potassium using the AutoAnalyzer system without the sampler (Table III). The standard deviation represents both sample and method variation. The sampling error is 0.008 or the difference between the sample plus method and the method variation.

Nine samples of the same tea were analyzed for potassium using the automated system, including the

samples using $0.5N$ NH₄C₂H₃O₂ with the following results: Technicon blade; 91, 75, 91, 77, and 75% and modified blade; 96, 94, 100, 99, and 98%. In general, the modified blade gave consistently higher recoveries, although there were some values below 98%.

Although the modified blade gives fairly good recoveries, it was felt that an extraction efficiency of 98% or better was necessary. Toward that end, increasing the temperature of the extracting solutions improved the extraction efficiency. For several solvents and temperatures, the results are given in Table II. The use of $0.5N$ NH₄C₂H₃O₂ at 50° C. was chosen over $0.35N$ HCl at 100° C. The latter solution is corrosive, and use of it near its boiling point would be quite difficult.

A study of the effect of grinding on particle size of tea leaf revealed that, under the conditions described above, an almost even weight distribution of ground leaf in the >40 mesh, 40–60 mesh, 60–80 mesh, and 80–200 mesh fractions with a small amount (about 7%) smaller than 200 mesh. Dried leaf has two main structures, veins (including stalk) and dried soft tissue, which respond differently to grinding action. Grinding

Table II. Evaluation of Extractants at Different Temperatures

Extractant	Potassium Recovery, %			
	25° C.	40° C.	50° C.	100° C.
Water	69	. . .	. . .	92
0.35N HCl	92	. . .	. . .	101
0.5N NH₄C₂H₃O₂	96	97	100	. . .

Table III. Analysis of Errors

Source of Error	Average	S.D.	95% C.L.
Ashed Samples			
Anal. method	1.84[a]	0.008	1.84 ± 0.02
Subsamples			
Sampling and anal. method	1.81[b]	0.016	1.81 ± 0.03
Solid Prep Sampler			
All	1.51[c]	0.017	1.51 ± 0.03

[a] Average of 1.84, 1.83, 1.85, and 1.84%.
[b] Average of 1.84, 1.81, 1.79, 1.81, and 1.80%
[c] Average of 1.48, 1.50, 1.51, 1.51, 1.52, 1.54, 1.50, 1.50, and 1.52%.

Table IV. Comparison of Results by Different Methods

Sample	1 Ashing	2 Manual HCl	3 Solid Prep $NH_4C_2H_4O_2$	4 Manual $NH_4C_2H_4O_2$
POTASSIUM OBTAINED, %				
A	1.82	1.80	1.88	1.81
B	1.95	1.88	1.94	1.84
C	1.76	1.74	1.83	1.78
D	1.85	1.75	1.82	1.79
E	1.65	1.54	1.66	1.62
DEVIATION FROM ASHED SAMPLES, %				
A	...	−1.1	+3.3	−0.6
B	...	−3.6	−0.5	−0.6
C	...	−1.1	+4.0	+1.1
D	...	−5.4	−1.6	−3.2
E	...	−6.7	+0.6	−1.8
Av. % Dev., %		−3.6	+1.2	−1.1

Table V. Potassium Content of Different Foodstuffs

Foodstuff[a]	Potassium, % Solid sampler	Control[b]
Mushroom	3.50	3.80
Celery	7.00	6.90
Pudding (instant)	1.88	2.20
Peas	0.75	0.75
Tomato soup	1.23	1.32
Alphabet vegetable soup	0.77	0.75
Potato soup	1.10	1.05
Coffee	1.70	1.79
Cream of mushroom soup	0.82	0.85
Cabbage	1.90	1.96
Beef noodle soup	0.70	0.73
Carrots	2.15	2.23
Onions	1.25	1.30

[a] All samples were dehydrated products.
[b] Samples ashed at 450° C. and potassium determined on the ash.

Table VI. Effect of Mesh Size on Extraction of Potassium Using AutoAnalyzer System

Foodstuff[a]	Potassium, % Large particles[b]	Small particles[c]	Controls[d]
Carrots	1.85	2.15	2.23
Coffee	1.58	1.70	1.79
Cabbage	1.68	1.90	1.96
Potato (diced)	0.64	0.79	0.75

[a] All samples were dehydrated products.
[b] Sample ground for 1 minute.
[c] Sample ground for 3 minutes.
[d] cf. Table V, note b.

Solid Prep sampler system, to test the reproducibility of the extraction procedure. The results of the potassium analysis ranged from 1.48 to 1.54% with a standard deviation of 0.017 (Table III). This deviation represents the error from the Solid Prep system, the analytical method, and the sampling error. The sampling error and the method error were each 0.008 as noted above. The difference between 0.017 and 0.016 represents the error due to the sampler, indicating that the sampler does not contribute a significant error to the procedure.

Comparison of Results by Different Methods. A series of samples was analyzed for potassium by:

1, ashing the sample and analyzing the extract; 2, manually extracting with HCl; 3, extracting directly from the tea leaf using ammonium acetate with Solid Prep sampler; and 4, manually extracting the samples with ammonium acetate. The results are presented in Table IV and are not meant to give statistical validity but to indicate some numerical support for the authors' method of choice.

The ashing technique was used as the control for calculating the per cent deviations for methods 2, 3, and 4. There is good agreement between the Solid Prep results and the ashing technique. The Solid Prep sampler results ranged from a +4.0% to −1.6% for analysis of different samples with an average of +1.2% higher than the ashing technique. Manual extraction with either $NH_4C_2H_3O_2$ or HCl gave results which were consistently lower than both sampler and ashing technique.

Applicability of Method to Other Foodstuffs. Preliminary tests on other foods were conducted using the general procedure as developed in this study. The results are listed in Table V. Preliminary studies show that this method is suitable for determination of potassium in most materials containing soluble potassium salts. The particle size effected the rate of extraction for certain materials as seen in Table VI. Potassium is extracted more slowly from larger particles. Therefore, the appropriate particle size must be determined for each food type.

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