Flame Photometric Determination of Alkali and Alkaline Earth Elements in Waters. I. Sodium and Potassium

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Introduction

It is our usual experience in a flame photometric determination of an element that when other elements and compounds co-exist they often interfere with that element, sometimes positively and other times negatively. The present investigation was commenced to develop sensitive methods for determining alkali and alkaline earth elements by making use of the positive interference phenomena toward one element in such a way that the determinable amount of that element is greatly lessened.

Thus the writers succeeded in establishing a more satisfactory method of determining sodium and potassium in which the minimum determinable amount is lowered to one-tenth for both these two elements in any comparison with the most sensitive methods hitherto proposed. A method for the simultaneous determination of calcium and strontium was also achieved in which the minimum determinable amount of strontium was lowered to one-tenth.

Determination of Sodium and Potassium

Preliminary Experiments.—Previous investigators have proved that the addition of methyl alcohol, ethyl alcohol or propyl alcohol to the solutions of gelatine and cane sugar increases the detectability of sodium and potassium in these solutions probably by intensifying the emissions of the two elements[1,2].

Based upon this information, and taking into consideration physical properties, the writers chose a number of alcohols, aldehydes and ketones. The same volume of one of these substances was added to a series of a solution containing sodium chloride or potassium chloride. Then the intensities of emissions of sodium and potassium in these solutions were determined with a Perkin-Elmer type flame photometer.

The results listed in Table I show that acetone, methyl ethyl ketone, propyl alcohol and ethyl alcohol are particularly effective and that the effectiveness decreases successively.

The next test was to compare the effectiveness by changing the added amount of these substances. It is evident from Fig. 1 that acetone is the most effective with the least amount added and that there is a particular range of concentration for each substance in which the effectiveness is the greatest.

The results also show that, as expected, the physical properties of the individual

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1) J.W. Berry, D.G. Chppel and R.B. Barnes, *Ind. Eng. Chem., Anal. Ed.*, 18, 19 (1946).

2) R.D. Catom, Jr. and R.W. Bremer, *Anal. Chem.*, 26, 805 (1954).

TABLE I

EMISSION INTENSITIES OF Na AND K IN NaCl SOLUTIONS (0.05 ppm FOR Na) AND IN KCL SOLUTIONS (0.4 ppm FOR K) IN THE ADDITION OF OTHER SOLVENTS IN SINGLE OR IN COMBINATION. BRACKETED VALUES ARE FOR Na. INTENSITY OF THE ORIGINAL SOLUTION IS 8–9 FOR Na AND 6–7 FOR K.

	Acetone	Ethyl alcohol	Propyl alcohol	Methyl ethyl ketone	Butyl alcohol	Formaldehyde	Acetic acid	Isooctyl phenol	Lauryl amine hydrochloride
Acetone	13 (20)								
Ethyl alcohol	13	9 (10)							
Propyl alcohol	35	18	9 (15)						
Methyl ethyl ketone	35	7	27	10 (20)					
Butyl alcohol	10	20	16	15	—				
Formaldehyde	10	5	11	—	—	7 (9)			
Acetic acid	18	15	14	12	10	25	8 (9)		
Isooctyl phenol	20	15	13	14	12	10	20	10 (–)	
Lauryl amine hydrochloride	20	12	10	15	18	—	10	8	14 (16)

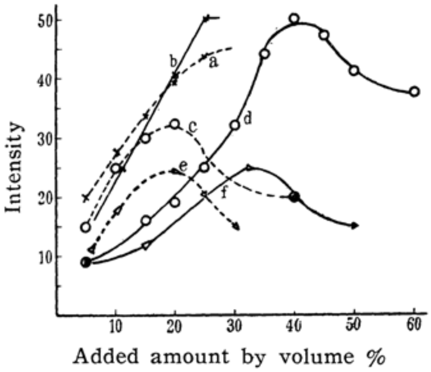

Fig. 1. Effectiveness of acetone, propyl alcohol and ethyl alcohol on the emissions of Na and K.

a	Acetone Na	b	Acetone K
c	Propyl alcohol Na	d	Propyl alcohol K
e	Ethyl alcohol Na	f	Ethyl alcohol K

substances are closely connected with the intensifying effect.

As shown in Table II, acetone which has the greatest interference is the greatest in heat of combustion, small in heat of vaporization as well as in sulface tension, and exceedingly small in viscosity.

TABLE II

PHYSICAL CONSTANTS OF THE SOLVENTS RECOMMENDED

	Surface tension dyn./cm.	Viscosity	Heat of combustion cal./g.	Heat of vaporization cal./g.
Acetone	22.5	2.9×10^{-3}	7400	132.1
Methyl ethyl ketone	18.1	3.9×10^{-3}	5831	124.1
Propyl alcohol	23.8	17.2×10^{-3}	4821	159.0
Ethyl alcohol	22.3	12.0×10^{-3}	7090	224.6

The circumstances are interpreted as follows: Its smallness in surface tension and in viscosity makes it easy for a large amount to pass into the flame as finely atomized. The small heat of vaporization makes easy the vaporization whereby the emission intensity is increased. And its large heat of combustion contributes considerably to raising the flame temperature.

A further test was made on the effect produced by the binary combination of the most effective substances. By Table I it is shown that the best results are obtained in two combinations, one of the acetone-methyl ethyl ketone and the other of acetone-propyl alcohol.

The next test was carried out by changing the amounts of the components in the system of acetone-propyl alcohol. The results in Table III show that the intensity is halved for propyl alcohol when the amount is reduced by one-quarter, while a 35% drop in intensity is first seen for acetone when the amount drops to one-half. This finding points to the

TABLE III

EMISSION INTENSITIES AT DIFFERENT COMPOSITIONS IN THE ACETONE-PROPYL ALCOHOL SYSTEM

Na ppm	K ppm	Acetone %	Pyropyl alcohol %	Intensity
0.05		20	40	40
0.05		10	40	32
0.05		20	30	20
0.05		0	0	8
	0.4	20	40	100
	0.4	10	40	65
	0.4	20	30	50
	0.4	0	0	6–7

fact that propyl alcohol is more essential to the intensifying action than acetone to the acetone-propyl alcohol system.

One point which must not be overlooked when acetone is applied to the flame photometry is that its relatively large amount might cause an incomplete combustion. As a matter of course the writers examined whether or not a part of the acetone in the acetone-propyl alcohol system could be replaced by ethyl alcohol. The examination shows that in order to keep the original degree of intensity, a large amount of ethyl alcohol is required (see Table IV).

TABLE IV

EMISSION INTENSITY FOR THE COMBINATION SYSTEM OF ACETON, PROPYL ALCOHOL AND ETHYL ALCOHOL

K ppm	Acetone %	Propyl alcohol %	Ethyl alcohol %	Intensity
0.4	15	40	20	100
0.4	15	40	25	100
0.4	0	0	0	6–7

Another approach to the positive interference is the addition of surface active agents. Two kinds of such agents, isooctyl phenol and lauryl amine hydrochloride, accidentally at hand, were tested.

The result (Table V) shows that at surface tension minimum, isooctyl phenol is more active than lauryl amine hydrochloride. However, the background of isooctyl phenol is considerably great. For this reason isooctyl phenol was rejected and the addition of lauryl amine hydrochloride at a concentration of 0.25% was recommended where it can give an intensifying effect with the least background comparable to isooctyl phenol.

TABLE V

EFFECTIVENESS OF SURFACE ACTIVE AGENTS

Agent	Concentration %	K ppm	Intensity	Background
Isooctyl phenol	0.5	0.4	32	20
Lauryl amine hydrochloride	0.25	0.4	16	1–2

The final experiment was to ascertain in the presence of this amount of lauryl amine hydrochloride to what extent the amount of propyl alcohol could be reduced with no heavy decrease in intensity. The answer was, as listed in Table VI, that the amount of propyl alcohol can be decreased to a concentration about 10% by an intensity decrease of 40% for sodium and 34% for potassium of the original values for the respective elements.

Hereupon arose another question: Can butyl alcohol replace at least in part the propyl alcohol? Primarily, butyl alcohol is more effective than propyl alcohol but because of its low solubility in water it has not been recommended by the writers. This situation was changed when lauryl amine hydrochloride was introduced. The introduction of this substance promises a great solubility of butyl alcohol in the system whereby the effectiveness of the system is considerably

TABLE VI

EFFECTIVENESS OF THE COMBINATION SYSTEM OF ACETONE, PROPYL ALCOHOL, BUTYL ALCOHOL, METHYL ETHYL KETONE AND LAURYL AMINE HYDROCHLORIDE

Na ppm	K ppm	Acetone %	Propyl alcohol %	Butyl alcohol %	Lauryl amine HCl %	Methyl ethyl ketone %	Intensity	gain
0.05		5	40	0	0.25	0	80	
0.05		5	30	0	0.25	0	70	
0.05		5	20	0	0.25	0	56	
0.05		5	10	0	0.25	0	48	
0.05		5	0	10	0.25	0	110	18:10
0.05		5	0	5	0.25	0	100	18:30
0.05		0	0	5	0.25	5	100	18: 8
0.05		0	0	0	0	0	10–11	18: 8
	0.4	5	40	0	0.25	0	80	
	0.4	5	30	0	0.25	0	75	
	0.4	5	20	0	0.25	0	60	
	0.4	5	10	0	0.25	0	55	
	0.2	5	0	10	0	0	60	
	0.2	5	0	5	0	0	45	
	0.4	5	0	5	0.25	0	100	20: 6
	0.4	0	0	5	0.25	5	100	20: 0
	0.4	0	0	0	0	0	6–7	

increased. The result of the examination actually evidenced that a system, 5% of acetone, 5% of butyl alcohol and 0.25% of lauryl amine hydrochloride, gives an intensity comparable to the highest value ever obtained among many combinations. Thus was established the system upon which the following analytical method of sodium and potassium determination is constructed.

Temperature Regulation in the Environment.—Table VII shows that the emission intensity drops by 17–23% when the thermometer, inserted in the space between the atomizer and the photometer cover, drops from 30°C to 10°C.

TABLE VII

INTENSITY OF EMISSION AND ENVIRONMENTAL TEMPERATURE

Na ppm	K ppm	10°C		30°C	
		Intensity	Gain	Intensity	Gain
20		100	12:68	100	11:25
10		100	13:27	100	13:47
2		100	17:28	100	17:68
0.1		100	21: 9	100	21:20
0.1		22±1	18:36	22±1	18:51
	2.0	60	21: 0	97	21: 0
	1.0	35	21: 0	50	21: 0
	0.4	12	21: 0	28	21: 0

Thus it is advisable in winter to heat the atomizer by placing an adjustable electric plate at the bottom whereby the constancy and consequently the accuracy of the meter reading are secured.

Stock Solutions.—Stock solutions are prepared different in concentration for sodium and potassium and different in their proportions. Here the maximum concentration is 10 ppm. for both sodium and potassium. The solutions are kept in polyethylene bottles with a cap.

Calibration Curves.—From the stock solutions several series of standard solutions are prepared as follorwed: To a suitable amount of the stock solution, 25 ml. of acetone, 25 ml. of butyl alcohol and 1.25 g. of lauryl amine hydrochloride are added. After shaking thoroughly, the solution is made up to 500 ml. Each series consists of solutions different in dilution but definite in the ratio Na/K. Then a calibration curve is made for each of these series (see Figs. 2 and 3).

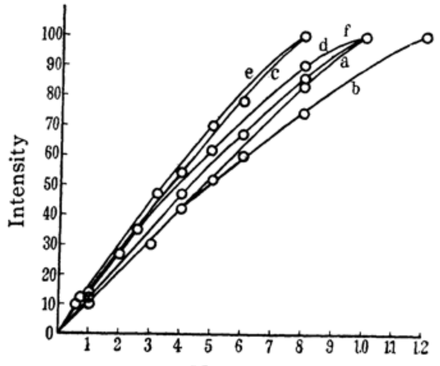

Fig. 2. Calibration curves for sodium at different Na/K. Ratios on the map are Na/K values for the individual curves.

a 1:1 b 3:1 c 4:1
d 5:1 e 8:1 f 10:1

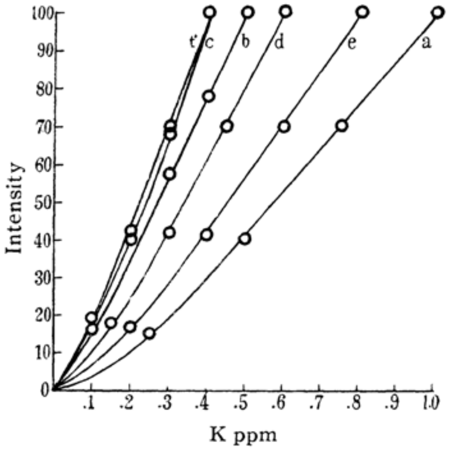

Fig. 3. Calibration curves for potassium at different Na/K. Ratios on the map are Na/K values for the individual curves.

a 1:1 b 3:1 c 4:1
d 5:1 e 8:1 f 10:1

Method of Processing Samples.—Originally the writers' attempt was to afford a method to meet the requirements for determining minor amounts of sodium and potassium as found in rain and other terrestrial waters in which both sodium and potassium are often found in quantities of 0.1 ppm or below. Thus the method of processing will be described so that it can easily be applied to such materials.

From a rain sample previously filtered through absorbent cotton and freed from all contamination such as soot and other dusts, an accurately measured amount (at least 40 ml.) is transferred to a 50 ml. measuring flask. To this are successively added 2.5 ml. of acetone 2.5 ml. of butyl alcohol and 2.5 ml. of a 5% aqueous solution of lauryl amine hydrochloride. After thorough shaking, the solution is made up to 50 ml., put to the flame photometer and the intensities of sodium and potassium are read.

Accuracy of Method.—The accuracy of the method was tested as follows: To rain water samples, the sodium and potassium contents of which were previously determined, a certain amount of sodium or potassium is added and sample content is determined.

As shown in Tabe VIII, for sodium the deviation of the observed value from the theoretical is from 0 to −8.6% with an average error −4.7%, while for potassium the deviation is from −1.9 to +7.5% with an average error +3.6%.

Interferences by Other Elements.—Among the interferences by other elements, those by

TABLE VIII

APPLICATION TO RAIN WATER AND ACCURACY OF DATA

Collected on	Fraction	Original content		Added		Theoretical		Found		Error in %	
		Na ppm	K ppm	Na ppm	K ppm	Na ppm	K ppm	Na ppm	K ppm		
July 23, '55	1	0.35	0.10	0.30	0.30	0.65	0.40	0.60	0.43	−7.7	+7.5
	2	0.45	0.11	0.30	0.30	0.75	0.41	0.75	0.41	0.0	0.0
	3	0.65	0.18	0.30	0.30	0.95	0.48	0.90	0.49	−5.2	+2.1
	4	0.50	0.10	0.30	0.30	0.80	0.40	0.78	0.43	−2.5	+7.5
	5	0.30	0.10	0.30	0.30	0.60	0.40	0.55	0.42	−8.3	+5.0
	6	0.23	0.075	0.30	0.30	0.52	0.375	0.50	0.38	−5.8	+1.4
	7	0.28	0..63	0.30	0.30	0.58	0.363	0.53	0.38	−8.6	+2.8
	8	0.30	0.081	0.30	0.30	0.60	0.38	0.58	0.38	−3.3	+0.26
Aug. 27, '55	2	0.35	0.24	0.30	0.30	0.65	0.54	0.63	0.53	−3.1	−1.9
	3	0.24	0.11	0.30	0.30	0.54	0.44	0.51	0.45	−5.6	+9.1
	4	0.20	0.18	0.30	0.30	0.50	0.48	0.51	0.49	−2.0	+2.1
								Average		−4.7	+3.6

TABLE IX

APPLICATION TO ONTOLOGICAL MATERIAL

Lymph of Animal	Sample taken mg.	Na ppm	K ppm
Internal ear Guineapig	0.59	85.5×10^3	13.5×10^4
External ear Guineapig	0.31	13.7×10^3	14.5×10^3
Internal ear Corpse (Labyrinthin fluids)	0.96	1.99×10^3	7.99×10^3
External ear Calf	1.22	2.05×10^3	3.98×10^3
External ear Shark	0.02	37.5×10^3	11.2×10^3

calcium and magnesium are particularly notable. The presence of 20 ppm. of calcium causes an error −2% to sodium and −1% to potassium, wile 25 ppm of magnesium causes an error −2% to sodium and −1% to potassium. Consequently, the method can be directly applied to ordinary fresh waters in which the portions of calcium or magnesium to sodium or potassium are not large. Other elements in the ordinary fresh waters show no interference.

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