# 17259. A New Method of Flame Photometry.*

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An adequate review of the principles and background of flame photometry is given in the papers of Barnes *et al.*[1,2]

In order to accomplish accurate quantitative analysis by flame photometry, the element to be determined must be in solution in the form of a salt and this solution must in some manner be atomized into a flame of *constant thermal output*, so that a *constant amount* of the solution is introduced into this flame *per unit time*.

All previous workers have utilized an atomizer-burner system which contained a chamber through which the atomized vapor of the solution passed before entering the exciting flame, and all commercial models of flame photometers which have been marketed in this country and abroad are based on this principle.

After working with such a chamber atomizer-burner system for many months, we found it impossible to obtain consistently reproducible and accurate quantitative results to within one per cent. Moreover, we could not consistently introduce a constant amount of solution into a flame per unit time. This was due mainly to the fact that when an aqueous solution is atomized and passed through a chamber, the size of the droplet particles which enter the exciting flame is not uniform. This factor is more or less uncontrollable, because the particle size and the rate of change of size are dependent upon numerous and variable physical conditions, among which are: (a) temperature of the atomizer chamber; (b) viscosity of the solution being atomized; (c) surface tension of the solution being atomized, and (d) certain

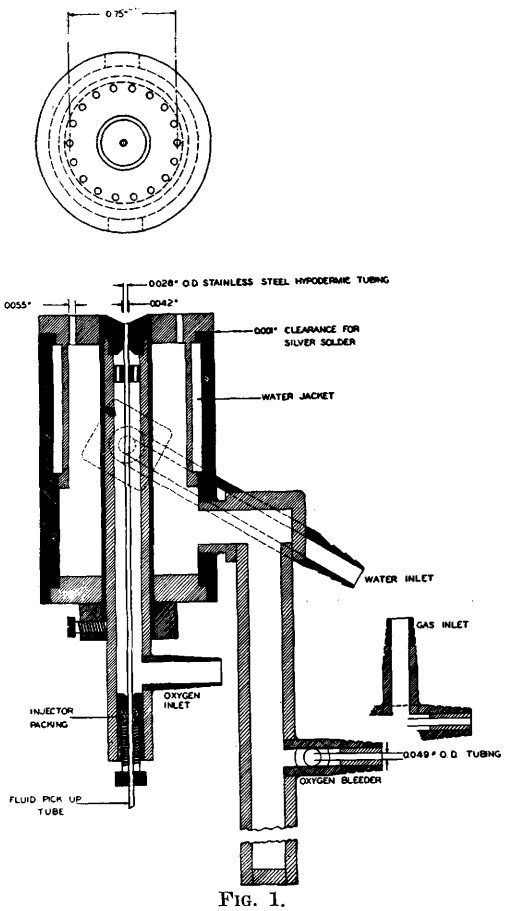


FIG. 1.
Diagram of Atomizer Burner System.

This system uses a mixture of illuminating or propane gas and oxygen for the thermal excitation of the atomized solutions. Atomization is accomplished by the use of oxygen under a constant pressure of 5 to 7 lbs., which enters the tube labeled oxygen-inlet and escapes at the narrow space below the fluid pick-up tube and the atomizer tip, producing a venturi effect, which accomplishes both the pick-up and atomization of the fluid to be analyzed. The fluid pick-up tube is immersed in a small glass beaker which contains the solution to be analyzed.

Approximately 0.75 ml of solution is atomized per minute, with a consumption of 11 cubic feet of oxygen per hour at 7 lbs. delivery pressure. To all solutions analyzed is added 0.04% STEROX SE (Monsanto Chemical Company), a non-ionic wetting agent, cation free, which overcomes the capillarity effects of the fluid pick-up tube.

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1 Barnes, R. B., Richardson, D., Berry, J. W., and Hood, R. L., *Indust. and Eng. Chem., Anal. Ed.*, 1945, **17**, 605.

2 Berry, J. W., Chappell, D. G., and Barnes, R. G., *Indust. and Eng. Chem.*, 1946, **18**, 19.

TABLE I.
Deviations of Sodium and Potassium Determinations in Urine and Plasma by the Present Method of Flame Photometry from Sodium and Potassium Determinations by Chemical Methods.

| Sodium | | | | | Potassium | | | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | Flame photometry, meq. | Gravimetric determin., meq. | Difference, meq. | Difference, % | No. | Flame photometry, meq. | Volumetric determin., meq. | Difference, meq. | Difference, % |
| 1 | 147.1 | 143.9 | +3.2 | +2.2 | 1 | 3.83 | 3.74 | +0.09 | +2.4 |
| 2 | 144.9 | 143.7 | +1.2 | +0.8 | 2 | 3.40 | 3.29 | +0.11 | +3.3 |
| 3 | 143.8 | 144.7 | —0.9 | —0.6 | 3 | 4.30 | 4.40 | —0.10 | —2.3 |
| 4 | 145.8 | 143.7 | +2.1 | +1.5 | 4 | 4.76 | 4.67 | +0.19 | +1.9 |
| 5 | 112.0 | 111.8 | +0.2 | +0.2 | 5 | 4.48 | 4.38 | +0.10 | +2.3 |
| 6 | 146.8 | 144.8 | +2.0 | +1.4 | 6 | 4.70 | 4.64 | +0.06 | +1.3 |
| 7 | 135.2 | 137.8 | —2.6 | —1.9 | 7 | 4.46 | 4.48 | —0.02 | —0.4 |
| 8 | 140.5 | 143.3 | —2.8 | —2.0 | 8 | 4.42 | 4.41 | +0.01 | +0.2 |
| 9 | 142.5 | 140.0 | +2.5 | +1.8 | 9 | 5.59 | 5.61 | —0.02 | —0.4 |
| 10 | 133.7 | 135.5 | —1.8 | —1.3 | 10 | 4.65 | 4.82 | —0.17 | —3.5 |
| 11 | 138.8 | 140.0 | —1.2 | —0.8 | 11 | 4.85 | 4.73 | +0.12 | +2.5 |
| 12 | 135.5 | 136.2 | —0.7 | —0.5 | 12 | 4.68 | 4.54 | +1.4 | +3.1 |
| 13 | 91.0 | 88.7 | +2.3 | +2.6 | | | | Avg error 2.0% | |
| 14 | 92.3 | 91.0 | +1.3 | +1.4 | | | | Range —3.5 to +3.3% | |
| 15 | 91.0 | 90.7 | +0.3 | +0.3 | | | | | |
| 16 | 180.8 | 178.1 | +2.7 | +1.5 | | | | | |
| 17 | 180.0 | 178.8 | +1.2 | +0.7 | | | | | |
| 18 | 176.0 | 178.8 | —2.8 | —1.6 | | | | | |
| 19 | 142.0 | 143.1 | —1.1 | —0.8 | | | | | |
| 20 | 144.0 | 145.0 | —1.0 | —0.7 | | | | | |
| 21 | 139.0 | 138.3 | +0.7 | +0.5 | | | | | |
| | | | Avg error 1.2% | | | | | | |
| | | | Range —2.0 to +2.6% | | | | | | |

electrostatic effects due to variations of charge on the chamber walls.

The above conclusions were reached primarily from visual observations of the atomization of certain solutions containing fluorescein, under illumination with filtered ultraviolet light, under various standard laboratory conditions. For these reasons we decided to abandon the chamber and devise an atomizer which permitted the direct and immediate combustion of the atomized droplets.

Mention must also be made of the rather well-known spectroscopic phenomena of mutual excitation. This is illustrated by the production of more luminous energy per meq. of potassium in the presence of a large excess of sodium than from potassium in pure solution. This difficulty may be overcome by using as standards solutions containing a ratio of interfering elements, which only approximate that in the solution analyzed. For instance, in the case of Na and K, there is a wide plateau of mutual excitation from 18 Na: 1K to 56 Na: 1K, wherein no increase of excitation occurs. A similar compensation is made for the less frequently observed phenomenon of quenching.

We have found it unnecessary to use an internal standard method with this atomizer-burner system. Direct experiment showed no interferences, such as reported by Barnes *et al.*,[1,2] from the presence in the solutions of the common inorganic acids up to 2% concentration, or of urea or sucrose up to at least 4% concentration.

Fig. 1 is a schematic illustration of the atomizer-burner system developed in order to achieve this result, and thus overcome the above mentioned difficulties. With this apparatus we have been able to introduce a constant amount of the atomized solution per unit time into a flame of constant thermal out-

put. Several different glass filter and interference filter photometric devices have been successfully utilized with this burner-atomizer system. These include a simple barrier layer photocell-suspension type galvanometer system, vacuum phototube-electronic voltmeter, and a direct current operated photomultiplier tube-suspension galvanometer system.

Comparison of the results of sodium and potassium determinations in urine and plasma by standard chemical methods,[3,4] with the method of flame photometry described herein, are shown in Table I. We do not believe that this comparison reflects the true accuracy of this method of flame photometry, but represents at the present time the only acceptable means of evaluation.

The reproducibility, duplicability and recovery of added sodium and potassium to urine and plasma are of the order ±0.5%. Further work is in progress for the determination of calcium, magnesium and other cations. Further data, as well as information as to the commercial availability of this instrument, will be available in a forthcoming publication.

*Summary.* A new type of atomizer-burner system is described for use in flame photometry which accomplishes consistently accurate quantitative chemical analysis of sodium, potassium, and other cations.

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[3] Butler, A. M., and Tuthill, E., *J. Biol. Chem.*, 1931, **93**, 171.

[4] Folch, J., and Lauren, M., *J. Biol. Chem.*, 1947, **169**, 539.

## 17260. Inhibition by Cyanide of Serum Alkaline Phosphatase in Normal Man, Obstructive Jaundice and Skeletal Disorders.

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It has been the general experience that marked increases in serum alkaline phosphatase activity occur consistently in only 2 disease categories in man: 1. in skeletal disorders associated with active, widespread proliferation of bone or cartilage, 2. in diseases of the liver or biliary tract with obstruction of the intra- or extrahepatic biliary channels.[1] There is general agreement that the high serum alkaline phosphatase levels observed in skeletal disorders are the result of augmented production of the enzyme by osteoblasts, which are known to be a prolific source. Opinion is divided as to the origin of the increased serum alkaline phosphatase in biliary tract obstruction. It would seem reasonable to suppose that since alkaline phosphatase is excreted in the bile and (being a large protein molecule) does not escape through intact glomeruli in man, retention of the enzyme in the plasma occurs when the excretory biliary channels are obstructed. There is, however, the possibility that the increased enzyme appearing in the plasma is of hepatic origin, and perhaps a different alkaline phosphatase from that responsible for most of the enzyme activity exhibited by the plasma of normal subjects and of those with skeletal diseases.

Drill and coworkers [2,3] reported that sodium cyanide in concentrations to 0.1M only slightly inhibited the serum alkaline phosphatase activity of normal dogs and man whereas the elevated levels in hepatic damage were markedly reduced, to approximately normal levels but not below. Their data were interpreted as indicating that the alkaline phosphatase appearing in the serum of dogs and man with hepatic damage is, for the most part,

[1] Gutman, A. B., Olson, K. B., Gutman, E. B., and Flood, C. A., *J. Clin. Invest.*, 1940, **19**, 129.

[2] Drill, V. A., Annegers, J. H., and Ivy, A. C., *J. Biol. Chem.*, 1944, **152**, 339.

[3] Drill, V. A., and Riggs, D. S., *J. Biol. Chem.*, 1946, **162**, 21.