

COMPARATIVE EVALUATION OF ANALYTICAL TECHNIQUES FOR THE QUANTIFICATION OF POTASSIUM IN FRUIT JUICES AND CORRESPONDING BEVERAGES

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Abstract

Chronological advancement in technology has introduced sophistication to analytical chemistry. This positive development was necessitated by the need to answer myriads of questions such as the degree of selectivity, cost effectiveness, accuracy, sensitivity, speed and versatility of the evolving techniques. This trend in increasing complexity constitutes a major threat to the earlier classical chemical methods, which, invariably being considered obsolete. This research effort aimed at unraveling the invalidity of this claim. In the study, classical chemical methods were exemplified by gravimetric and titrimetric analytical techniques, while the modern physico-chemical methods were exemplified by flame emission and atomic absorption spectrophotometric techniques. These techniques were applied in quantifying potassium in fruit juices expressed from five selected tropical fruits namely: Apple(pome spp),Ginger(zingiber officinalis),Lemon (citrus orantifolia) and Orange(citrus reticulata).The result was evaluated using standard deviation and co-efficient of variation. The four representative techniques used were able to quantify the element of interest (potassium) and were also quite comparable in terms of sensitivity, specificity, selectivity, precision and accuracy.

Introduction

The superiority of the accuracy and precision of the instrumental technique over the classical techniques has for long been a subject of contention among the analytical chemists. Wilson (1962) pessimistically opined: 'time may come when gravimetric and titrimetric methods of determination will only be of historical interest as other methods such as solvent extraction, ion exchange and of course various instrumental method which need no tedious preliminary separation and which of course combine identification with determination". This assertion, if valid, may defeat the whole essence of fundamental chemical analysis. Analysts cannot shy away from verifying a method by a standard reference material as well as estimating the composition of the material. In these cases, the gravimetric technique is highly employed (Beck, 1991, Valcarel, 1995). The titrimetric analysis involves the application of fundamental principle of stoichiometry, thermodynamics and chemical equilibria (Beck, 1991 and Valcarel, 1995).

An attempt at comparing analytical methods must bear in mind a suitable substance that could tolerate the application of various analytical techniques. Potassium is an element of choice based on this description. This attribute has made potassium element relevant in the comparison of various analytical techniques in chemical science.

Potassium is one of the most determined elements, being a chief constituent of animals and vegetable intracellular fluids. It has a complimentary function with sodium in the extra cellular fluids in the animal living cells. Potassium determination is a useful index for estimating fruits for fruit juice content of food products (Pearson, 1976). Potassium is also a valuable content of fruit, milk, meat, vegetable, legumes and in fertilizer compounding. It is also an important element in the soil for uptake by plants. Healthwise, deficiency and excessiveness of potassium constitute serious

problems. These are medically referred to as hypokalemia and hyperkalemia respectively. These conditions can be brought about through dietary intake and/or other numerous circumstances (Kornan, 1965). In the quantitative assay of potassium, a lot of techniques have been used (Kohler, 1953), Sporek and Williams (1955) have used tetraphenylborate in complexing potassium in gravimetric analysis. Both titrimetric and gravimetric procedure involving Chloroplatinate have also been used to determine potassium in fruit juice as stipulated by (A.O.A.C, 1995). It has also been well established that such instrumental techniques as Atomic Absorption Spectrophotometry (AAS), Atomic Emission Spectrophotometry (AES), Flame Atomic Absorption Spectrophotometry (FAAS) and Flame Atomic Emission Spectrophotometry (FAES) quantified potassium in fruits and fruit juices to high degree of success A.O.A.C (1995) and Zuchetti, (1993)

The aim of this study is to validate or prove otherwise that the assertion that the classical techniques are no longer relevance as analytical methods. The study also aimed at comparing both classical chemical methods with modern instrumental method along with possible modifications to upgrade their efficiencies. The comparisons are orientated towards their relative specificity, sensitivity, accuracy precision, speed, and versatility and cost effectiveness.

Materials and Methods

Collection of samples

Samples of fresh fruits were obtained from four major fruit markets in Lagos. The corresponding fruit juice beverages were selected among fast selling beverage products also in Lagos.

Table 1: Food and beverage samples used in the analysis

Fruits Common Name	Corresponding Botanical Name	Beverage Product
Tropical Apple	Pome specie	Crown Apple Juice
Ginger	Zingiber officinalis	Fanta Ginger Ale
Lemon	Citrus orantifola	Limca Lemon Drink
Orange	Citrus reticulata	Gold Spot Orange
Pine-Apple	Ananas comosus	Thymas Pine Apple Juice

Sample preparations

Cut pieces of the sample of each of the fruits were put in a clean white cloth, which was squeezed to express the juice. Mixture of concentrated Nitric Acid and Perchloric Acid (Middleton and Stuckey, 1953) was used to digest all the samples. The choice of this method is because it is less time consuming and controllable from abnormal violence.

Instrumental determination of potassium

The analytical instruments: Atomic Absorption Spectrophotometer (A.A.S.) and the Flame Emission Spectrophotometer (F.E.S) were used. 5g of each sample digest were made to 50 cm³ for the quantification of potassium in both instruments. Standard concentrations of potassium solutions were prepared from Analar^R grade Potassium Chloride. These were done to obtain calibrations for the test samples.

Classical methods of determining potassium

Gravimetric Analysis: The samples' digests were further heated in order to obtain concentrates. Tetraoxochlorate VII (Perchloric) Acid (60% w/w) in mixed butan-1-ol and pure Ethylethanoate

ester were reacted with the digest concentrate (Beck, 1991). Precipitates were obtained. The potassium contents were then evaluated.

Titrimetric Analysis: The sample digests were heated further to almost dryness. sodium Cobaltinitrite complex solutions were added to the digest and titrated with of $0.05 \text{ mole dm}^{-3}$ potassium permanganate (Beck, 1991). The potassium contents were evaluated stoichiometrically.

Recovery of techniques used

Samples were prepared to obtain recovery as a measure of accuracy of the techniques used. Standard addition method was used as follows: 1000ppm of potassium iodide solution was prepared by weighing 4.256g of Analar grade Potassium Iodide and dissolving it in de-ionised water. The volume was made to 1 dm^3 mark of the volumetric flask. 1 cm^3 of the Potassium Iodide which corresponded to 1 mg of potassium was pipetted and dropped on the sample digest prepared from 5g of the raw sample. This is the new re-try sample. The four methods were re-run with the new re-try samples.

Results and Discussion

Comparable values were obtained with respect to the amount of potassium in each sample analysed. The sample recoveries of all the techniques ranged between 98.56-99.01 %. This attests to their high accuracies of all the four techniques. All methods revealed specificities. The flame emission method is specifically amenable for alkali metal (Middleton and Stuckey, 1953). The technique employed the flame source of excitation, which was not as intensive enough as to cause excitation in most other elements in other groups. The atomic absorption possessed a similar high degree of specificity for the potassium metal; though atomic absorption is known to offer a wide range of detect ability for metals. As a matter of fact, the technical principle employed the use of source lamp tubes (Sydney, 1968) for a particular element – hence potassium element was detected by use of potassium source tubes.

Use of Cobaltinitrite complex as suggested by Piper (1984), showed that potassium could be specifically detected ruling out interference of ions of calcium, magnesium, aluminium, sulphate, phosphate and chlorides as well as some alkali metals like Lithium, sodium, Rubidium and Caesium. In the same manner, the Perchloric method chosen for the gravimetric analysis also ruled out the interference of chloride, Nitrate, tartarates, Borates and phosphate of sodium and lithium.

All the four techniques used had high measure of sensitivity to detect even the little quantity presence of potassium as was demonstrated by the low traces observed in beverage products. These instrumental techniques were quite versatile in this attribute. They have been shown to detect as low as part per billion presences of metals (Sydney, 1968). However, the sensitivities of the classical techniques were of appreciable magnitude. The chosen cobaltinitrite route for the titrimetric has once been shown (Smith, 1925) to be sensitive to as low as the range of 0.08 mg to 42 mg. The gravimetric technique was able to determine the low potassium load in fruit juice beverage.

The standard deviation and relative precision (co-efficient of variation) values expressed in percentage depicted high precision for all the techniques used. By this, it is implied that the techniques had less degree of variability of their outputs in the repeated determinations. In other words, there is a marked display of less vulnerability to error in all the techniques used. Precision of the AAS and FES was improved as suggested (BSI, 1995) by setting the wavelength of the

instrument to 766.5nm and mixing sample with caesium chloride to final concentration of 0.04g per dm³ prior to analysis. This adjustment was also able to reduce interferences.

The choice of tetraoxochlorateVII (perchloric) procedure (Wilhard, 1972) was a major enhancer of its reproducibility. The procedural modification (Piper, 1984) of the titrimetric method was by addition of concentrated sodium chloride solution followed by rapid addition of the agents in situ, under a carefully standardized conditions. This was responsible for reproducibility of the cobaltinitrite procedure for titrimetry.

The accuracy of all the four techniques used was comparable and of high degree with all the methods used. The study showed that recovery percentage of the analytical techniques was above 96 per cent. The automation process in instrumental technique had a contribution to the accuracy only a little above the classical techniques. This edge was a less significant methodic error, which was likely to have occurred along the procedural stages in the classical technique. The automation in the instrumental technique has short-cut many processes that would have been done manually in the classical procedure.

Conclusion

The foregoing exercise showed that the four techniques were able to determine the element of interest (potassium), both in the natural fruit juice and fruit juice beverages. The quantity of potassium was more substantial in the natural fruit juice than in the commercially processed fruit juice beverages samples. All the techniques were able to quantify as low as 0.62mg of potassium per 100mg of the sample. This study is of great significance in fact that though the classical techniques may be more laborious, they are still techniques of choice when accuracy, specificity, precision, selectivity and cost are needed to be weighed against the monopoly of sensitivity and time-savings of the Instrumental techniques. The future analytical challenges should therefore be directed towards modifying and modernizing the classical techniques based on rational and sound chemical principles of the classical techniques. The study also revealed that locally accessible, cheap and natural fruit juices can be a very good alternative to the expensive and capital intensive processed juice beverages in sourcing essential nutrients like potassium.

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Table2: Summary of Potassium load (mg/100g) in selected samples of fruit juices and corresponding fruit juice beverages

	A.A.S			F.E.S			TITRIMETRY			GRAVIM
	Mean	Std	Co-eff	Mean	Std	Co-eff	Mean	Std	Co-eff	Mean
	Mg/100g	%	%	Mg/100g	%	%	Mg/100g	%	%	Mg/100g
Apple fruit juice	33	2.5	189	35.8	1.1	0.77	33.15	5.16	0.78	30.2
Apple Fruit Juice Bev	410	2.9	0.7	2.3	1.3	1.6	4.08	3.33	1.64	3.88
Ginger Fruit Juice	100.6	2.2	0.54	113.8	1.1	0.24	97.9	2.25	0.11	96.4
Ginger Fruit Juice	1.9	2.1	1.8	2.31	1.9	0.82	1.84	1.37	1.48	2
Lemon Fruit Juice	33	2.4	1.82	38	1.5	0.99	32.75	4.47	0.68	31.3
Lemon Fruit Juice Bev.	0.62	1.5	2.46	0.7	1.3	1.76	0.82	1.37	3.37	0.82
Orange Fruit Juice	54.6	1.8	0.83	62.4	1.2	1.22	43.25	4.47	0.52	41.05
Orange Fruit Juice Bev.	0.82	1.6	1.98	1.02	0.8	0.4	0.98	0.89	1.83	0.82
Pine-apple Fruit Juice	41.5	2.7	1.63	50	1	0.4	50.65	2.73	0.27	51
Pine-appleFruitJuice Bev.	14.2	1.6	2.81	17.8	1.1	1.55	14.19	3.14	0.44	13.88