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Review of sodium analysis proficiency test results

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Abstract

Proficiency testing results for sodium analysis in foods raised concerns over the proportion of laboratories achieving satisfactory z-scores. Test materials for sodium analysis include fruit juice, canned meat meal, tomato sauce, cheese & pasta meal, and snack food. Fruit juice and tomato sauce data sets are the most problematic in deriving the assigned value with sufficiently low uncertainty to provide evaluative z-scores. The standard deviation for proficiency is derived from Horwitz, with a lack of collaborative trial data for these matrices to provide other guidance. The status of accreditation for the method/matrix does not appear to influence the observed variation in results. Microwave digestion is much less commonly used than simple acid digestion. The choice of determination method appears to be entirely matrix-dependent (whether flame atomic absorption spectroscopy, flame photometry or ICP spectroscopy). Results for juice matrix may be overestimated if flame photometry is used, either due to potassium interference or careless reporting where potassium is also determined.

Keywords:- Sodium, proficiency test, methodology, fruit juice, food

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Introduction

FAPAS[®] is the Food Analysis Performance Assessment Scheme, a proficiency testing service for food analysis laboratories. At the 37th FAPAS[®] advisory committee meeting in October 2009, a discussion paper was presented concerned with the observed low percentage satisfactory scores in sodium analysis proficiency tests (PTs). Analysis of sodium in cheese & pasta meals had been of particular concern, with 60-74% satisfactory scores for the five most recent tests. All tests had applied the robust mean as the assigned value and used the Horwitz equation for the standard deviation for proficiency. The question raised was, should there be a wider standard deviation for proficiency?

The statistical advice was that there was no justification for deviating from the use of Horwitz to derive the standard deviation. However, there was clearly still a problem. This author was tasked with further investigating sodium analysis, in relation to published collaborative trial data, and to look at the PT data and make comparisons with the homogeneity data. Is there any methodological basis for poor analysis or skewed data that can be addressed?

One of the rationales for conducting sodium analysis is the concern over health effects of consuming too much salt in the diet. The United Kingdom Food Standards Agency (FSA) publishes a list of high salt-containing foods (FSA 1) and the targets for reduction of salt levels in them. The recently revised target date is 2012 and tomato ketchup, for example, has a target level of 1.83 g salt 100g⁻¹ of ketchup (or 730 mg sodium 100g⁻¹) maximum. The FSA advises adults to consume no more than 6 g salt per day (FSA 2).

This paper describes the data sets from FAPAS[®] sodium PTs across five matrices (fruit juice, canned meat meal, tomato sauce, cheese & pasta meal, and snack food). The methods used by participants are presented and the problematic data sets are discussed.

Literature review

Five publications report collaborative trial data but none are particularly relevant to the matrices used in the FAPAS[®] PTs. Table 1 summarises the published information and each paper is briefly discussed in this review. A further publication discusses the results of another PT scheme but for water analysis (data not included in Table 1).

A study by the International Office of Wine (OIV) was briefly summarised (Junge 1987). Sodium was determined by flame photometry and by atomic absorption spectrometry (AAS). Both techniques had a linear correlation of reproducibility with concentration, with formulae of $R = 4.7 + 0.08C$ (flame photometry), $R = 2.5 + 0.054C$ (AAS). Flame photometry was unsatisfactory between laboratories so not recommended at the limit value of 60 mg L^{-1} . Reproducibility for AAS was 3.0% for white wine at 90 mg L^{-1} , 6.9% for red wine at 18 mg L^{-1} , 3.0% for dessert wine at 69 mg L^{-1} .

The technique of ion chromatography was discussed from the results of the third (2000) Aquacon freshwater interlaboratory exercise (Mosello et al. 2004). Although not a food, there are some interesting comparisons made for methodology. No details were provided for analytical results. However, expected consensus values for sodium were $2.25 \pm 0.1 \text{ mg L}^{-1}$ (sample A) and $3.70 \pm 0.1 \text{ mg L}^{-1}$ (sample B). Ion chromatography for cation analysis was only 20 – 30% of all methods, the main method being AAS. Reproducibility for ion chromatography for all cations was 6.6 – 19.0%. The best obtainable reproducibility was about 10% for IC water analysis at the concentrations used. There were no significant differences in precision between anion and cation IC analysis. Reproducibility in the study was comparable with previous studies for various matrices. IC results were highly comparable to AAS, AES, and ICP-ES. One important source of error is thought to be non-linearity of calibrations and infrequent calibration.

A special report summarised the findings of various studies into the precision parameters of analyses at nutritional levels (Horwitz et al. 1992). Macronutrients

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2
3 were defined as existing in foods above concentrations of about $10 \text{ mg } 100\text{g}^{-1}$.
4
5 Horwitz used his own equation to determine Horwitz Ratio (HorRat) values (the
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7 observed RSD divided by the RSD predicted by the Horwitz equation). Values at or
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9 above 2.0 indicate unacceptable method precision. Instrumental methods have
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11 simplified sodium analysis, although titration is still used by some laboratories. The
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13 recommendation is to restrict titration to levels greater than $0.1 \text{ g } 100\text{g}^{-1}$. One study
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15 was entirely excluded from this report due to potential inhomogeneity, at $1 \text{ g } 100\text{g}^{-1}$
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17 in cereal. External factors such as contamination probably give rise to sporadic high
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19 RSD_R . Emission spectroscopy is not well suited at less than 1000 mg kg^{-1} . Method
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21 complexity is not a factor governing the distribution of precision of interlaboratory
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23 assays. The report lists the contents of a database of precision parameters,
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25 covering the results of the various studies that were accepted by the authors. The
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27 overall results are summarised in short tables. For sodium, 129 datasets gave an
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29 average HorRat value of 0.94 (0.77 median) for a concentration range of $0.002 - 13$
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31 $\text{g } 100\text{g}^{-1}$. At a 90% interval, this provides RSD_R of $0.6 - 14\%$.

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33 A method originally validated by collaborative study for milk-based infant formula
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35 was extended to other types of matrix (Cook 1997). Eight collaborators returned
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37 results for ready-to-feed soy, soy powder, whey powder and casein-based enteral
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39 formulae. The method was dry ashing, followed by AAS determination. The
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41 concentrations varied from 238 to $2090 \text{ } \mu\text{g g}^{-1}$ with RSD_R from 3.0 to 6.7% . Average
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43 RSD_R estimate was 4.7% , compared to 9.2% in the original study in milk-based
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45 formulae.

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48 Milk products were revisited for a new FAAS standard method by ISO/IDF (Noël et
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50 al. 2008). A prior small study found that different digestion techniques for milk
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52 products were not statistically different. However, most participants used microwave
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54 digestion followed by dry ashing. 16 samples (eight different samples in blind
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56 duplicate) were presented with 18 lab returns. A control sample for training was
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58 included. Sodium in the products had mean values of $1.74 - 16.8 \text{ g kg}^{-1}$ (excluding
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60 acid casein) with HorRat values $0.9 - 1.8$. A parallel study used ICP-OES which was

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3 found to be essentially equivalent. The FAAS method is published as ISO 8070
4 (ISO/IDF, 2007).
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10 The Nordic laboratories conducted their own interlaboratory study for sodium only in
11 a variety of foods by wet microwave digestion with FAAS (Julshamn et al. 2005).
12 Several references demonstrated that microwave digestion was a suitably rapid
13 technique for complex samples. Blind duplicate samples were of broccoli, carrot,
14 bread, Saithe fillet, pork and cheese, which followed a pre-trial test using bovine liver
15 and non-fat milk powder CRMs. The method is applicable to dry or wet foods. Nine
16 laboratories reported results. Mean values ranged from 1480 – 8260 mg kg⁻¹ with
17 RSD_R of 4.2 – 6.9%. HorRat values were 0.9 – 1.6, therefore providing acceptable
18 precision.
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28 One study of the flame photometric method suspected that the presence of
29 potassium in the sample might enhance the apparent level of sodium (Chen et al.
30 2005). Of 48 foods analysed for sodium (“salinity”), many had enhanced response
31 when artificially dosed with 1 µg g⁻¹ potassium solution (matrix concentration
32 dependent on dilution factor for analysis, equivalent to about 500 mg 100g⁻¹). A
33 lesser effect was observed with calcium but at 100 µg g⁻¹ calcium solution added.
34 Unfortunately, there is a poor explanation of why this may be the case, confusing
35 atomic and ionic forms. The effect may not be observed with only incurred
36 potassium, since sample preparation/dilution may reduce the amount of potassium
37 present to a point where it does not enhance the signal of sodium.
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49 **FAPAS® PT data**

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51 Although the FAPAS® series 25 tests in cheese & pasta meal were the original
52 source of concern over sodium reporting, sodium is a determinand in a number of
53 matrices. Data were collated from the following tests;
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- 57 • Series 08 fruit juice (“juice”) tests 0820, 0823, 0824, 0827, 0828, 0831, 0832.
- 58 • Series 01 canned meat meal (“meat”) tests 0146, 0154, 0156, 0159, 0161,
59 0163, 0166.
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- Series 20 tomato sauce (“tomato”) tests 2010, 2014, 2018, 2024, 2032, 2042, 2051, 2059, 2067.
- Series 25 cheese & pasta meal (“cheese pasta”) tests 2515, 2533, 2544, 2554, 2566.
- Series 25 snack foods (“snack”) tests 2531, 2537, 2547, 2558, 2569.

The number of tests used in the investigation per matrix is simply an indication of the historic extent of a particular test. Tables 2a, 2b, and 2c summarise the PT data (assigned values, standard deviations, percentage satisfactory scores). Full details are available in each individual test report (FAPAS®).

The juice test materials were alternately apple and pineapple juice, from commercial sources. The bulk test material was mixed for two hours before sub-sampling into glass bottles and retort pasteurised. Meat test materials were prepared from commercial ready-made meat meals, with various additions of rice, water and salt. The bulk mixed test material was chopped into a smooth paste before sub-sampling into cans and steam retorting. The tomato test material was from commercial sources and the bulk was mixed over a period of about 16 hours. Sub-samples in pots were stored at –20 °C prior to distribution. The cheese pasta test material was based on commercially available ready-made macaroni in cheese sauce meals. Additional ingredients were variously added, such as salt, butter and egg. The bulk mixed test material was chopped into a smooth paste before sub-sampling into cans and steam retorting. The snack test material was prepared from commercially available packets of snack foods, such as tortilla chips. The bulk material was milled and mixed before sub-sampling into foil sachets. The sealed sachets were stored in dry ambient conditions until distribution.

Differences in storage of test materials will reflect not only the stability of the matrix in question but also the other determinands in the test. All the tests reviewed here are for multiple determinands (for example, ash, moisture, pH, other metals). All test materials underwent homogeneity testing prior to distribution for the test itself.

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3 Again, although sodium is the analyte of interest in this review, all determinands
4 were subjected to homogeneity testing. The procedure for determining sufficient
5 homogeneity follows that used routinely by FAPAS[®] (Fearn and Thompson 2001).
6 All the test materials had sufficient homogeneity such that any sample to sample
7 variation would have a negligible effect on z-scores. The accumulated experience of
8 running these PTs suggests that the test materials are stable over the duration of the
9 test.
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18 Many of the tests for sodium also require chloride as a determinand. Instructions to
19 participants clearly state that sodium and chloride are to be reported independently,
20 i.e. that sodium must not be reported as sodium chloride. Apart from reporting
21 results, participants have the option to also report their method details.
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28 **Methods used by FAPAS[®] participants**

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30 The method details returned by participants were compiled for each matrix. The
31 method parameters were categorised into three groups; status of accreditation of the
32 method, method of digestion of the sample, and final determination technique.
33 Responses for the question of accreditation were simply either yes or no. The
34 sample digestion category was divided into three parameters – acid digestion,
35 microwave digestion, and other. Acid digestion assumes that microwave was not
36 additionally used. Finally, the determination technique was divided into four
37 parameters – flame atomic absorption spectroscopy (FAAS), flame photometry,
38 inductively coupled plasma (conventional and MS detection), and other. Figures 1a-
39 c chart the method responses.
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51 The principal observations can be summarised as follows. A larger proportion of
52 laboratories are not accredited for sodium in tomato sauce vs. the other matrices.
53 Juice has the highest proportion of microwave digestion of all matrices. Each matrix
54 has a very different determination method profile. Although the proportion of
55 accredited laboratories is lowest for tomato sauce, this does not account for the
56 problematic data observed for juice. There are no significant differences between
57 accredited and not accredited laboratories, except for two cheese pasta tests (2554
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3 and 2566) and one tomato test (2032) (T-test P-value < 0.05). The accreditation
4 status of sodium analysis does not appear to be a major factor in the results.
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10 A multi-variate approach was applied to the determination technique (all matrices)
11 and the digestion method for juice and tomato. No factors were evident for the
12 determination technique for meat, cheese pasta, snack or tomato. Method
13 responses were insufficient for tomato digestion methodology to provide an
14 adequate investigation of significance. The juice determination method investigation,
15 however, did show up an apparent trend. Determination by flame photometry
16 appears to overestimate, compared to FAAS, ICP and other methods (see Table 3).
17 For PT 0827, there is a significant difference (T-test, P-value < 0.05) in the mean
18 results for FAAS and flame photometry and similarly between flame photometry and
19 ICP. There are no significant differences between FAAS and ICP. For PT 0824,
20 there is a significant difference between flame photometry and ICP but not between
21 FAAS and flame photometry. There are no other significant differences between
22 results for different determination methods for any of the remaining juice tests.
23 There was no significant difference between acid digestion and microwave digestion
24 results for PT 0827.
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39 **Discussion**

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41 The juice PT data sets all use the mode for the assigned value, and three of the
42 seven tests were issued for information only, i.e. z-scores provided but on an
43 advisory (not evaluative) basis only. This was due to the high uncertainty of the
44 assigned value. Histograms of z-scores were dominated by skews to the high end.
45 One of these (0820) is due to careless potassium and sodium reporting swapped by
46 participants. Juice tests often require potassium as a determinand, which is present
47 at much higher levels than sodium (typically 50 times more). None of the
48 subsequent tests indicate that this remains a problem of misreporting. The meat
49 tests were largely problem-free, although the percentage satisfactory scores were
50 not great at 63-77%. For the purposes of this review, "satisfactory" is used to
51 describe z-scores within the range ± 2 , although it should be noted that the
52 terminology is advisory, not definitive. Tomato tests had more information only
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3 reports (four of nine tests) than cheese pasta or snacks (no information only reports),
4 and the homogeneity testing was more prone to weak analytical variance. Between
5 sample variance was, however, always acceptable. All tomato datasets were
6 actually fairly multi-modal, even the ones reported using the robust mean or median.
7 Cheese pasta tests were all essentially unimodal. Snacks tests were similarly fairly
8 unimodal, except test 2531 which was noticeably multi-modal. Juice satisfactory
9 scores were much worse (44 – 67%), and tomato had a wide range of satisfactory
10 scores (56 – 79%). Snack test scores were reasonable (60 – 82%); cheese pasta
11 tests have the narrowest range of satisfactory scores (60 – 74%). The juice test
12 results are the most worrying, with skewed and modal data sets, as well as low
13 percentage satisfactory scores.
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26 Generally, the homogeneity mean value is well within ± 2 z-scores. Although the
27 homogeneity mean value does not usually influence the assigned value, it can be a
28 useful indication of where different methodology provides a different result or where
29 there is a stability issue. One of the cheese pasta tests (2515, April 2004) had a
30 homogeneity mean just above +2 z-scores. This was also the poorest percentage
31 satisfactory result of all the cheese pasta tests (60%). One of the snack food tests
32 (2547, July 2007) had a homogeneity mean value well above +2 z-scores (but within
33 +3). However, this was the one snack food test that applied the mode as the
34 assigned value, with a distinctly multi-modal distribution. Comparison of the
35 homogeneity mean values with the assigned values does not raise any concerns for
36 these tests.
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48 Do laboratories testing different matrices apply different methodologies? A
49 comparison was made of the same laboratories across the five matrices (one recent
50 test per matrix). 18 laboratories participated in 3 or 4 matrices (none in all five
51 matrices). Virtually all laboratories use the same method for each matrix but usually
52 only up to three matrices tested for, and not all laboratories provide method
53 information for all tests. Only one laboratory, testing four matrices, used titration for
54 meat and FAAS for everything else. Only five of the 18 laboratories were tomato
55 testing laboratories. The number of tomato testing laboratories is much fewer than
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4 for other matrices (generally half as many) and they tend to test perhaps only one
5 other matrix. Only four of the 18 laboratories achieved all z-scores within ± 2 . One
6 laboratory consistently achieved negative z-scores in three matrices (snack, tomato
7 and meat). One laboratory consistently achieved negative z-scores in four matrices
8 (snack, cheese pasta, tomato and meat). Otherwise, there were no consistent
9 results.
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17 One further possible effect may be related to the different test materials' affinity for
18 picking up sodium from laboratory glassware or solvents. The liquid test materials
19 fruit juice and tomato sauce might be expected to be more prone to this and, hence,
20 account for their results distributions. However, the pH of both apple juice and
21 tomato sauce (FAPAS[®], e.g. 0832 and 2067) is about 3.6 so might be expected to
22 have a similar affinity for sodium from glassware. These two test materials share a
23 similar proportion of acid digestion sample preparation compared to other methods,
24 but the results distributions are different. It is unlikely, however, that sodium leaching
25 from glassware or solvents would significantly affect the result at the concentrations
26 being measured.
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37 Are the tomato tests only of interest to tomato-producing countries? Juice, meat and
38 tomato tests all have about one-third of participant countries being the UK. For
39 tomato tests, the UK plus Italy and Spain account for 58% of the participants. Of the
40 UK participants for juice, meat and tomato, about one-third do not submit results for
41 sodium (results for other determinands are submitted). Cheese pasta and snack test
42 participants are predominantly UK (47% and 46%, respectively) with 10% and 18%
43 of UK participants not submitting sodium results. This suggests that these latter two
44 matrices are only really important to UK eating habits. The largest participation by
45 far is for meat with about 100 participants per test (all determinands), followed by
46 juice with about 70. Cheese pasta and snack tests have the fewest participants.
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57 Most of the collaborative trial data (Table 1) are based on AAS determination. This
58 technique accounts for about one third of participants' methodology. None of the
59 collaborative trials are particularly relevant to the matrices used in the FAPAS[®] PTs.
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There do not appear to have been any published collaborative trials on sodium analysis in tomato products or fruit juice. However, the concentration of sodium in the PTs between about 0.5 and 1% has an observed RSD_R of about 5% (from standard deviation of results, data not shown). This is in keeping with that observed for the collaborative trial data.

Chen et al (2005) briefly discussed the possibility of potassium interfering in sodium determination by photometry. For tomato tests, which were noticeably problematic data sets, only 20% of methods reported used photometry. One test, 2067 (May 2009), had no methods reporting the use of photometry. The tomato PT data were not particularly skewed, and potassium was not a reportable determinand. It seems unlikely that potassium interference had an effect on tomato results. Juice, however, sometimes does require potassium to be reported (as well as sodium) and potassium can be 50 times higher than sodium in the test material. Sodium results in juice are often skewed to the high end. On only one test (0820, June 2006), this was obviously due to many laboratories misreporting their sodium and potassium results. Potassium interference in photometry determinations may, therefore, be a factor in over-reporting sodium. Again, only about 20% of juice methods used photometry. However, there appear to be no published works on studying potassium interference in photometry applied to food analysis.

Conclusions

Although cheese pasta tests first raised the question of satisfactory performance in sodium analysis proficiency tests, fruit juice and tomato sauce matrices are actually much more problematic. Efforts to encourage reduction of salt in the diet must be supported by good analytical data, and the PT results indicate problems with sodium analysis. There is a lack of appropriate collaborative trial data for the PT matrices, which may provide some insight into optimising the methodology. The lack of accreditation for tomato methods compared to the other matrices does not appear to influence the variation of results. The results of the tomato data appear to be random, however the juice data may be overestimated if flame photometry is used. Laboratories would be advised to avoid this technique for juice, in favour of FAAS or

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3 ICP methods. It would be desirable, albeit expensive to the cost of running the PT,
4 to obtain the assigned value by reference analysis for juice and tomato.
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9 10 **References**

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1 Sodium PT review, Sykes 2010
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4 **Table captions**

5 Table 1. Summary of sodium collaborative trial data
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7 Table 2a. Summary of sodium FAPAS[®] proficiency tests (fruit juice, canned meat
8 meal, tomato sauce)
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10 Table 2b. Summary of sodium FAPAS[®] proficiency tests (cheese pasta meal and
11 snack food)
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13 Table 2c. Summary of sodium FAPAS[®] proficiency tests (comments and
14 observations on selected tests)
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16 Table 3. Mean values by determination method for juice and tomato matrices (n
17 results)
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19 **Figure captions**

20 Figure 1a. Accreditation of sodium methods of FAPAS[®] participants
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22 Figure 1b. Sodium digestion methods of FAPAS[®] participants
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24 Figure 1c. Sodium determination methods of FAPAS[®] participants
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Review of sodium analysis proficiency test results

Mark Sykes, Bhavna Parmar, Michael Knaggs

Figure 1a

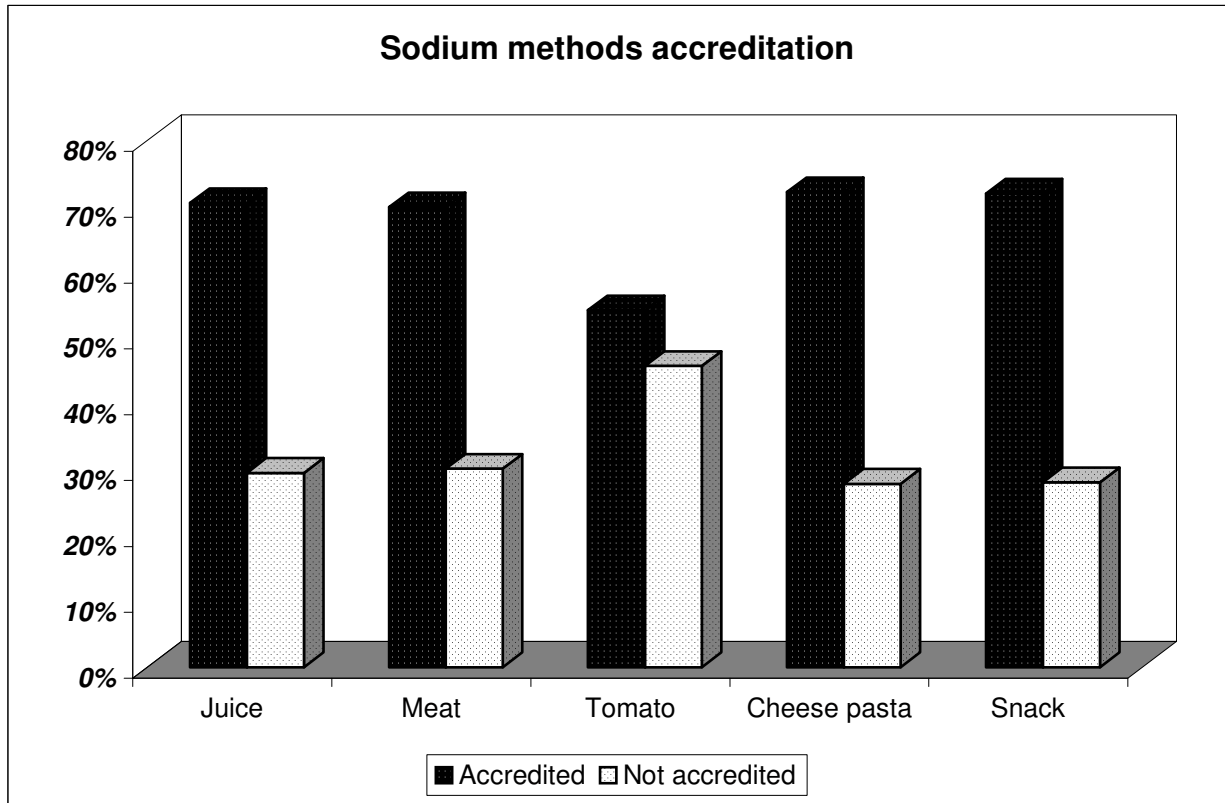
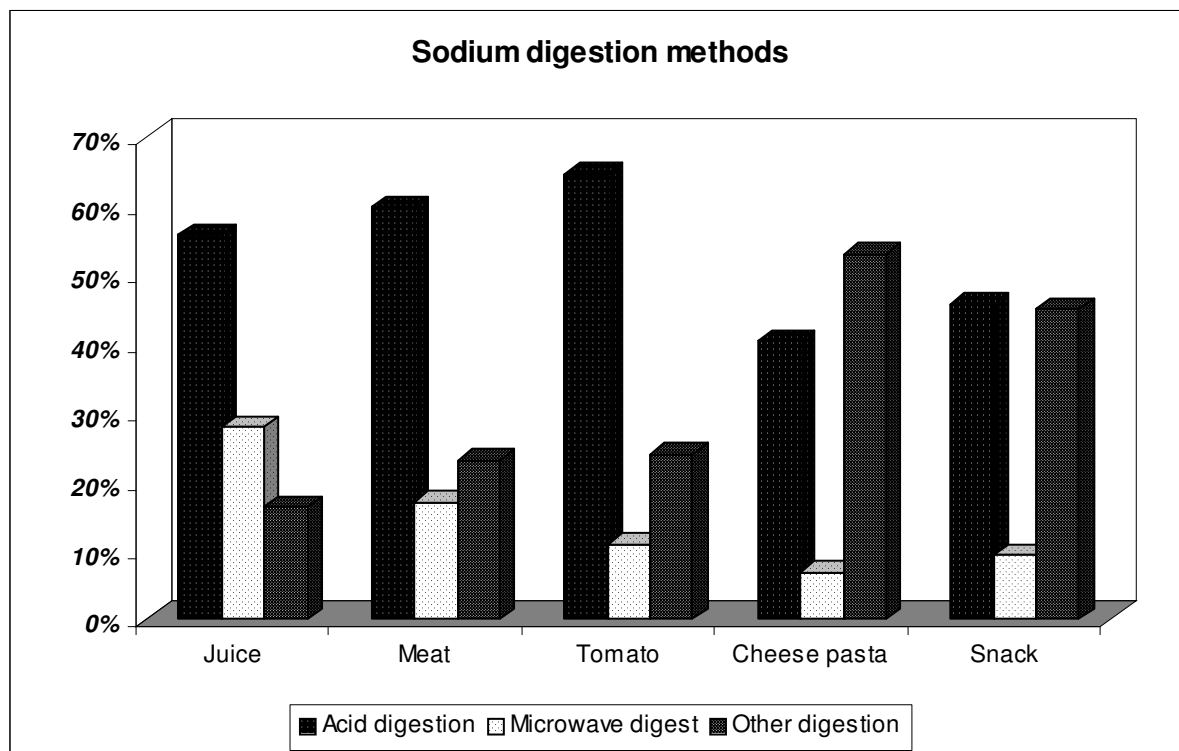
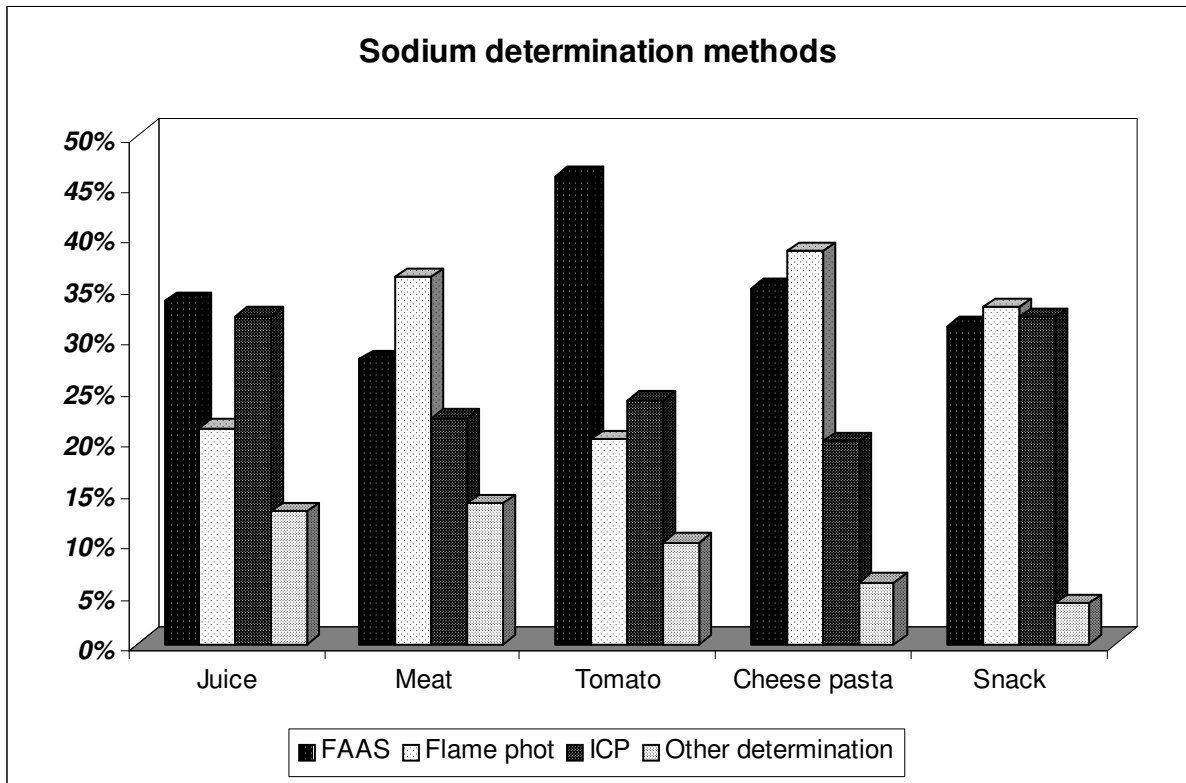


Figure 1b



Review Only

Figure 1c



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4 **Table 1. Summary of sodium collaborative trial data**

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Matrix	Conc.	Units	RSD _R	H RSD R	HorRat	Method
White wine	90	mg L ⁻¹	3.0	8.1	0.4	AAS
Red wine	18	mg L ⁻¹	6.9	10.4	0.7	AAS
Sparkling wine	69	mg L ⁻¹	3.0	8.5	0.4	AAS
White wine	89	mg L ⁻¹	4.8	8.1	0.6	Flame photometry
Red wine	18	mg L ⁻¹	12.3	10.4	1.2	Flame photometry
Sparkling wine	69	mg L ⁻¹	5.0	8.5	0.6	Flame photometry
General	0.002 - 13	g 100g ⁻¹	0.6 - 14		Note 1	Various
Seifen formula	544	µg g ⁻¹	3.7	6.2	0.6	AAS
Fatty, Note 2	312	µg g ⁻¹	3.0	6.7	0.4	AAS
Fatty paired, Note 2	238	µg g ⁻¹	5.8	7.0	0.8	AAS
Fatty powder paired, Note 3	2090	µg g ⁻¹	4.3	5.1	0.8	AAS
Seifen powder formula	1290	µg g ⁻¹	6.7	5.4	1.2	AAS
Infant milk powder	4.34	g kg ⁻¹	7.0	4.5	1.5	FAAS
Infant milk powder	2.99	g kg ⁻¹	8.6	4.8	1.8	FAAS
Infant milk powder	4.05	g kg ⁻¹	7.36 Note 4	4.6	1.6	FAAS
Infant powder	6.3	g kg ⁻¹	7.5	4.3	1.7	FAAS
Infant protein conc.	1.74	g kg ⁻¹	9.2	5.2	1.8	FAAS
Processed cheese	8.17	g kg ⁻¹	3.6	4.1	0.9	FAAS
Processed cheese	6.06	g kg ⁻¹	7.0	4.3	1.6	FAAS
Processed dried cheese	16.8	g kg ⁻¹	4.0	3.7	1.1	FAAS
Coccolli	2290	mg kg ⁻¹	5.0	5.0	1.0	FAAS
Coccolli	3540	mg kg ⁻¹	4.2	4.7	0.9	FAAS
Coccolli	8260	mg kg ⁻¹	4.4	4.1	1.1	FAAS
Coccolli	2030	mg kg ⁻¹	6.1	5.1	1.2	FAAS

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4	1480	mg kg ⁻¹	6.7	5.3	1.3	FAAS
5	5380	mg kg ⁻¹	6.9	4.4	1.6	FAAS

6: HorRat average value 0.94 (0.77 median), 129 samples listed in the reference

7
8: Ready-to-feed infant formula

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10: Infant formula

11: Derived from quoted HorRat. RSD_R is 47.2 in the reference but must be an error? Quoted HorRat is 1.6, Horwitz RSD_R is

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Table 2a. Summary of sodium FAPAS[®] proficiency tests (fruit juice, canned meat meal, tomato sauce)

Round	Test Material	<i>n</i>	Assigned Value	AV	Target RSD _R %	σ_p	Total No. of z-scores
0820	Apple Juice	24	20.95	mode*	10.12	2.12	32
0823	Pineapple Juice	26	54.6	mode	8.76	4.78	26
0824	Apple Juice	47	42.05	mode	9.11	3.83	48
0827	Pineapple Juice	35	15.68	mode*	10.57	1.66	37
0828	Apple Juice	44	25.86	mode	9.805	2.54	47
0831	Pineapple Juice	17	14.83	mode*	10.66	1.58	18
0832	Apple Juice	58	21.10	mode	10.11	2.13	58
0146	Canned Meat Meal	59	0.262	h15	4.9	0.013	60
0154	Canned Meat Meal	50	0.27	h15	4.87	0.01	51
0156	Canned Meat Meal	60	0.377	h15	4.63	0.02	62
0159	Canned Meat Meal	56	0.190	h15	5.136	0.00975	57
0161	Canned Meat Meal	55	0.871	h15	4.084	0.0356	56
0163	Canned Meat Meal	60	0.269	h15	4.874	0.0131	61
0166	Canned Meat Meal	60	0.175	h15	5.2	0.00910	61
2010	Tomato Sauce	26	1.07	h15	4.0	0.0424	26
2014	Tomato Sauce	33	1.32	h15	3.8	0.0506	34
2018	Tomato Sauce	20	0.86	h15*	4.7	0.04	21
2024	Tomato Sauce	32	1.21	h15	3.9	0.0471	32
2032	Tomato Sauce	23	1.075	h15	3.96	0.0425	23
2042	Tomato Sauce	16	1.27	mode*	3.86	0.0490	18
2051	Tomato Sauce	15	1.168	median*	3.91	0.0456	16
2059	Tomato Sauce	18	1.249	h15	3.87	0.0483	19
2067	Tomato Sauce	18	0.4286	h15*	4.54	0.0195	18

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3 also notes on table 2b.
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Table 2b. Summary of sodium FAPAS[®] proficiency tests (cheese pasta meal and snack food)

Round	Test Material	<i>n</i>	Assigned Value	AV	Target RSD _R %	σ_p	Total No. of z-scores
2515	Cheese & Pasta Meal	41	0.48	h15	4.4	0.0213	42
2533	Cheese & Pasta Meal	49	0.676	h15	4.24	0.0287	49
2544	Cheese & Pasta Meal	47	1.00	h15	4.00	0.0401	47
2554	Cheese & Pasta Meal	42	0.663	h15	4.25	0.0282	43
2566	Cheese & Pasta Meal	50	1.020	h15	3.99	0.0407	52
2531	Snack Food	21	1.27	h15	3.9	0.0490	23
2537	Snack Food	38	1.379	h15	3.811	0.0526	38
2547	Snack Food	33	0.79	mode	4.15	0.0326	35
2558	Snack Food	26	0.6592	h15	4.259	0.0281	27
2569	Snack Food	27	0.5471	h15	4.380	0.0240	27

its are mg L⁻¹ for juice, g 100g⁻¹ everything else.

n is number of results used in calculation of the assigned value (AV)

AV is assigned value calculated as robust mean using Huber's h15

assigned value issued for information only assessment, due to significant uncertainty of the assigned value.

matrices use Horwitz for the standard deviation for proficiency (σ_p).

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Table 2c. Summary of sodium FAPAS[®] proficiency tests (comments and observations on selected tests)

Round	Test Material	Comment
0820	Apple Juice	Six labs misreported Na and K; causes high skew
0823	Pineapple Juice	Slightly skewed to high end but mode closer to homogeneity than robust mean
0824	Apple Juice	High skew but only 2 labs may have misreported Na and K. Unimodal distribution
0827	Pineapple Juice	Skewed to high end but K not reportable. Culled Na unimodal distribution
0828	Apple Juice	High skew but K symmetrical, no misreporting. Essentially unimodal distribution
0831	Pineapple Juice	Few results, high skew, no K. Major mode AV but many minor modes above this
0832	Apple Juice	Opposite Na and K skews not due to reporting. Major mode AV plus high minor modes
2018	Tomato Sauce	Trimodal distribution
2042	Tomato Sauce	Mode has high uncertainty
2051	Tomato Sauce	Median better than robust mean but still high uncertainty
2059	Tomato Sauce	Questionable uncertainty of robust mean
2067	Tomato Sauce	Robust mean best but has high uncertainty
	Cheese & Pasta	
2515	Meal	Homogeneity mean just above +2 z-scores
2531	Snack Food	Fairly modal distribution

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2537	Snack Food	Verging on bimodal distribution
2547	Snack Food	Homogeneity mean above +2 z-scores. Modal distribution
2558	Snack Food	Unimodal distribution
2569	Snack Food	Unimodal distribution

canned meat meal essentially unimodal and symmetrical. Homogeneity okay, compares well to AV.
tomato datasets are multi-modal to a greater or lesser degree.
Cheese pasta tests fairly unimodal distributions.

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Table 3. Mean values by determination method for juice and tomato matrices (n results)

Matrix	FAAS	Flame photometry	ICP	Other
Juice /mg L ⁻¹				
1	22.8 (4)	48.9 (6)	31.3 (6)	18.8 (1)
2	59.3 (4)	90.3 (3)	60.0 (8)	62.8 (3)
3	52.0 (18)	66.6 (4)	42.0 (10)	44.2 (4)
4	18.2 (8)	52.8 (7)	15.8 (7)	17.2 (5)
5	33.4 (12)	38.8 (8)	25.2 (9)	24.8 (5)
6	14.7 (5)	20.6 (1)	25.3 (5)	21.5 (2)
7	26.9 (13)	31.7 (7)	26.1 (19)	21.0 (4)
8				
9				
10	1.07 (11)	1.08 (3)	1.06 (6)	1.03 (4)
11	1.30 (13)	1.29 (7)	1.32 (10)	1.42 (3)
12	0.837 (7)	0.873 (4)	0.933 (3)	1.01 (4)
13	1.23 (9)	1.21 (5)	1.23 (4)	1.36 (2)
14	1.08 (7)	1.10 (4)	1.10 (3)	1.06 (4)
15	1.28 (5)	1.40 (3)	1.28 (1)	1.34 (4)
16	1.51 (1)	1.18 (2)	1.28 (4)	1.11 (6)
17	1.31 (3)	1.22 (3)	1.26 (3)	1.21 (6)
18	0.406 (7)	N/A (0)	0.362 (4)	0.502 (4)