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Solid sampling atomic absorption spectrometry and matrix composition of organic reference materials

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Abstract

In solid sampling atomic absorption spectrometry, reference materials (RM) are not only used for internal quality control, but also to make calibration curves. The last application may be divided into the usage of the RM's directly by weighing different amounts, and the usage of the RM as a base for standard addition.

In using biological reference materials or materials of biological origin, a classification and critical review can be useful. In this paper classification based on the inorganic matrix content of the certified reference materials of BCR is suggested.

INTRODUCTION

Biological materials may vary widely, as may be expected when one realizes that the paraphrase biological materials includes all animals from protozoe to the blue whale, and all plants from bacteria to the redwood. Biological materials vary physically from fluids with 90% or more water content, as in the case of transport media as blood or invertebrates and sea plants, until solid material as bone or tree bark with a water content of 50% or less. Organic content of biological materials varies widely from simple alcohols and acids through sugars, proteins until DNA.

For solid sampling AAS, however, the inorganic matrix composition is more important than the organic matrix. It is known in conventional graphite furnace AAS that the inorganic matrix composition may depress the analyte peak heights. Examples are the influence of Na on the determination of Al in liquified animal tissue, human serum and urine (1). However, this influence of Na could not be established in another paper (2), where the L'vov platform was used in combination with the graphite furnace. Here an influence of high concentrations of $MgCl_2$, and $CaCl_2$ when using aged platforms could be observed on the determination of Al.

Also in slurry atomization graphite furnace AAS problems may arise due to matrix influences. Examples are given by Stephen et al. (3) where for the BCR Certified Reference Material Single Cell Protein (CRM 273) too low concentrations were found in some elements. Differences ranged from minus 11% for Zn via minus 21% for Pb until minus 38% for Cd at a concentration level of 30-40 µg/kg.

The most comprehensive examples of problems will be given for solid sampling, as this is the subject of the colloquium. Grobecker and Klüssendorf (4) found different Pb values in two spiked species, i.e. crab, and mussels. For crab material 88% (8 µg/kg) too much was found, for mussel material 23% (89 µg/kg) too much, if compared with the expected concentration. Also for Hg a too high concentration was determined: in tuna fish they found plus 34% (59 µg/kg), if compared with the

expected concentration. Atsuya et al. (5) found too low values for Cu in NIST pine needles. With peak area calculation they found minus 7%, with peak height minus 26% at a concentration level of 3 mg/-kg, thus at a considerably higher concentration levels than the authors mentioned before. Aaseth et al. (6) reported problems in the Se determination due to thermal instability. They solved this problem by addition of a silver or nickel powder matrix modifier. Klein et al. (7) found too low Pb values in NIST Bovine Liver 1577, BCR bovine liver CRM 186 and BCR bovine kidney CRM 187. They found minus 6%, minus 18%, and minus 10% at concentration levels of 0.3-0.5 mg/kg.

Frech and Baxter (8) found minus 59% (at 2 mg/kg) Al in NIST bovine liver 1577a. These observations were in agreement with those in the papers of Couri et al. (1) and of Manning et al. (2), and could be due to the influence of the matrix compound Na. In another paper, Baxter and Frech (9) found that Co influenced Pb in the = 261.4 nm non resonance line and that in case a continuum source was used as background correction system, AlCl (gas) molecules were responsible for undercorrection. As the authors mentioned before used Zeeman background correction systems, this miscorrection due to AlCl molecules could not be the case in these papers. Baxter and Frech (9) found for different materials, i.e. red cabbage, bovine liver and green cabbage different concentrations when using different calibration standards, i.e. tomato leaves, standard addition or aqueous.In case of NIST Tomato leaves 1573 they found minus 1-14%. The best results were obtained with the addition of a matrix modifier consisting of $Mg(NO_3$ + $Pb(NO_3)_2$ + 0.04% Triton- x 100, a standard addition method and an atomization temperature of 2400°C for the Perkin Elmer cup-in-tube technique. Although it might be expected that in another system specially equipped for solid sampling analysis, i.e. Grün, some problems are not appearing, it will be clear that not all problems will disappear.

BIOLOGICAL REFERENCE MATERIALS

Biological reference materials may be used in solid sampling AAS either to check the accuracy, or for calibration purposes. For both purposes beside the microcomposition of the analytes, the homogeneity and the matrix composition should be known.

The microcomposition is of course the existing ground for reference materials certified for trace elements in biological materials. Regarding the homogeneity it has been described that there exists a relation between the test amount and the standard deviation (10). Other authors will deal with this aspect more comprehensively (11,12). Regarding the matrix composition it may be stated that within the spectrometric system this factor is dominating together with the temperature program.

As a first attempt to classify the different existing biological reference materials, the Certified Reference Materials of BCR are reviewed (13). A great advantage for users of materials of BCR over materials of other suppliers is that for every single material comprehensive reports are available. In these reports both the certified concentrations and assayed concentrations are given together with the determination methods used as well as the statistical methods used for computation.

The following materials are available (Table 1). These materials may be classified into the following groups according to physiological similarity:

- animal 184,185,186,278
- fresh water plants 60,61
- solid land plants 62,100,101,129
- seawater plant 279
- single cell protein 273
- nutrients 63,189,191

Table 1

Number	Name	Ref	Number	Name	Ref
60	Lagarosiphon major (aquatic plant)	14,15	185	Bovine liver	21
61	Platyhypnidium ripa (aquatic plant)	14,15	186	Pig kidney	21
62	Olive leaves	14,15	189	Whole meal flour	20
63	Skim milk powder	16,17	191	Brown bread	20
100	Beech leaves	18	273	Single cell protein	22
101	Spruce needles	18	278	Mussel tissue	23
129	Hay powder	19	279	Sea lettuce	24
184	Bovine muscle	21			

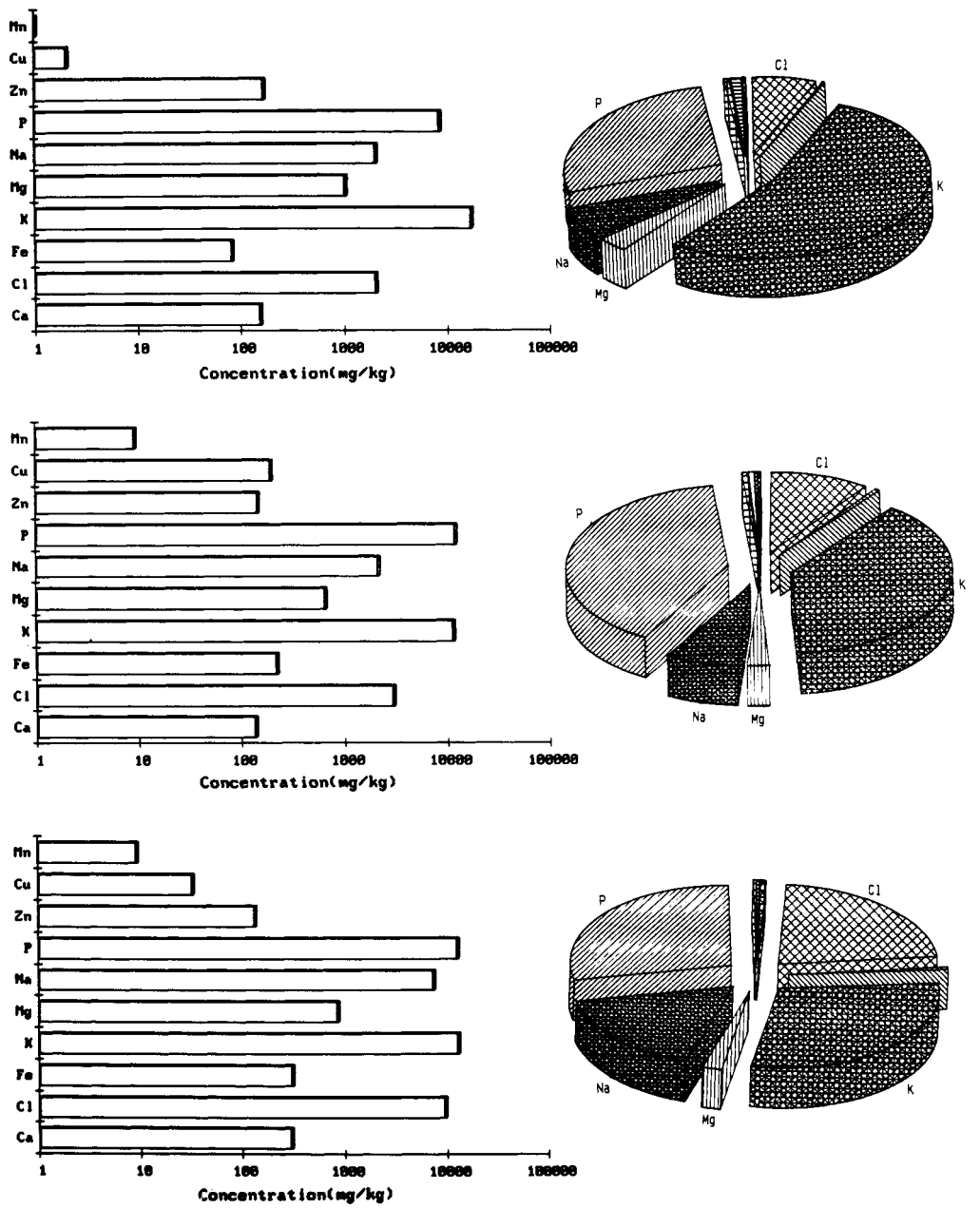

Fig. 1 a CRM 184 bovine muscle b 185 bovine liver c 186 pig kidney

CONCLUSIONS OF USAGE OF BRM's

In Figures 1-5 the CRM's are classified into groups mentioned earlier; bar and pie model Figures are made. The bar model enables the overview over all determined elements whereas the pie model gives more insight regarding head components. In the Figures, only the major constituents are mentioned. It should be noted, that a pie model gives only an accurate impression if the total amount of the major constituents will be 100%.

The first peculiarity is that in the materials not all major constituents are determined, e.g. sodium is not determined in material 100, 101, and 129.

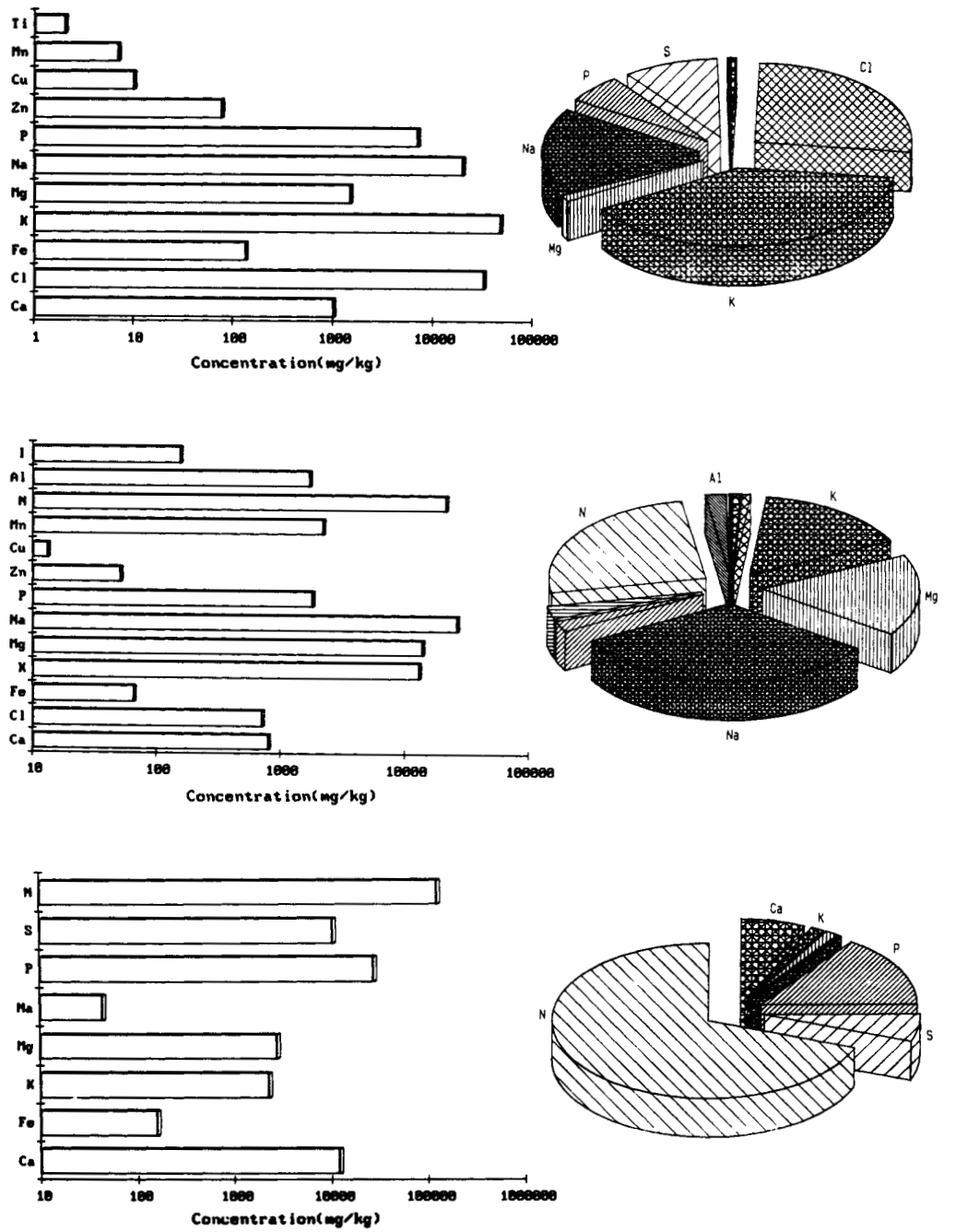

Fig. 2 a 278 muscle tissue b 273 single cell protein c 279 sea lettuce

Another important constituent element determined in a part of the materials only, is chlorine. This element is not determined in material 129 and 273. It may be stated, that to compare reference materials, all major constituents should be determined above the mg/kg level.

Another, minor problem, is that some of the element concentrations are mentioned as oxide (e.g. Na_2O), while in other materials the concentration is given as Na. Uniformity should here to be preferred. If we compare the different materials and keep in mind that in literature mentioned before some

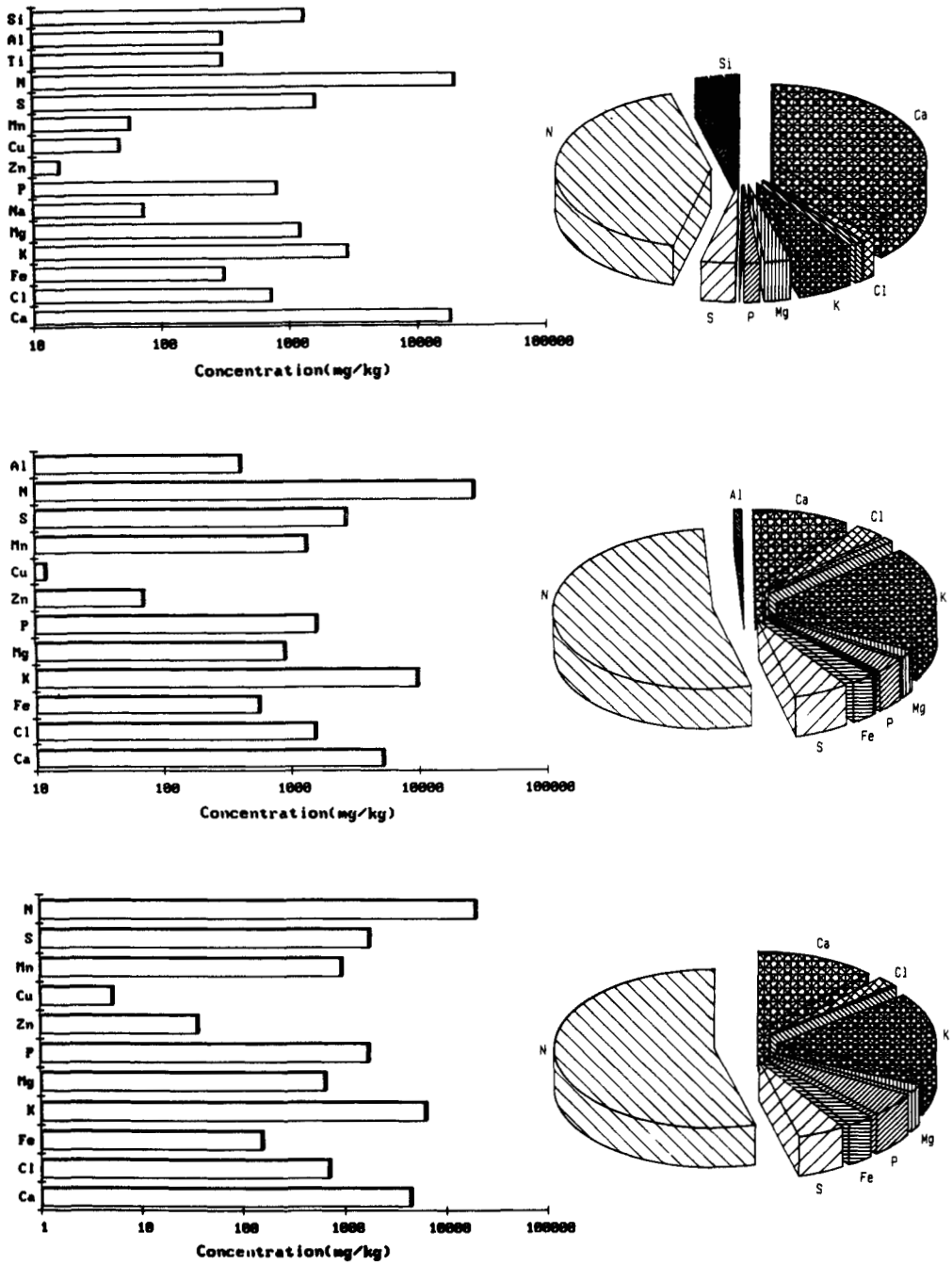

Fig. 3 a 62 olive leaves b 100 beech leaves c 101 spruce needles

problems regarding matrix effects comprehensively were mentioned, it wil be clear that materials containing large amounts of silicium are useless for SS-AAS. Materials 60, and 61 are to be classified within this category. In vegetable materials containing Si, e.g. materials 100, 101, 129, and 279, this element was not determined. Another important element is sulphur as sulphide. This element is given in the 6 materials 60, 61, 62, 100, 101, 129, ad 273, but not in the other materials.

Calcium and magnesium, also important peak depressing elements, are always determined thus for these elements a good choice can be made between the materials.

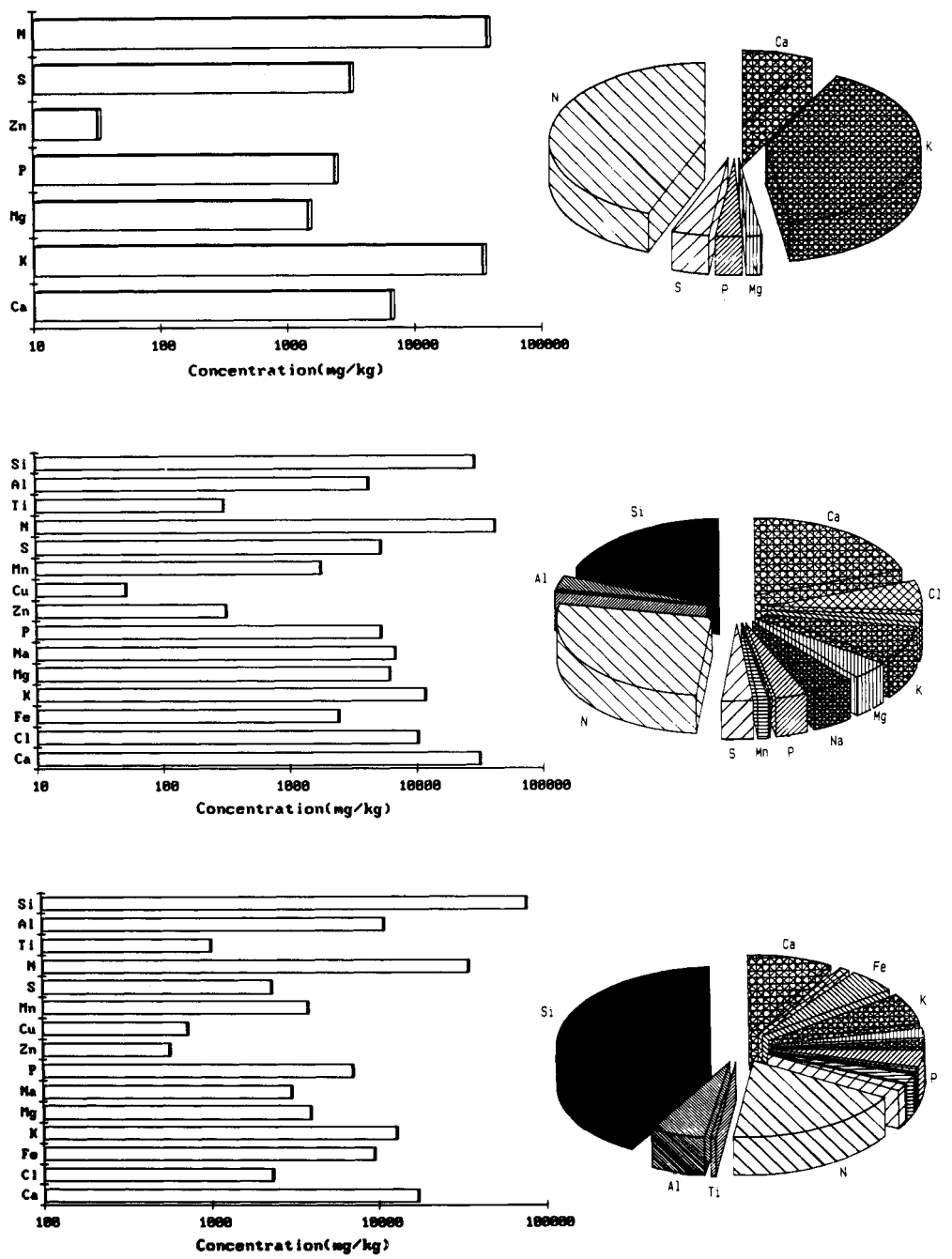

Fig. 4 a 129 hay powder b 60 Lagorosiphon c 61 Platyhypnidicum

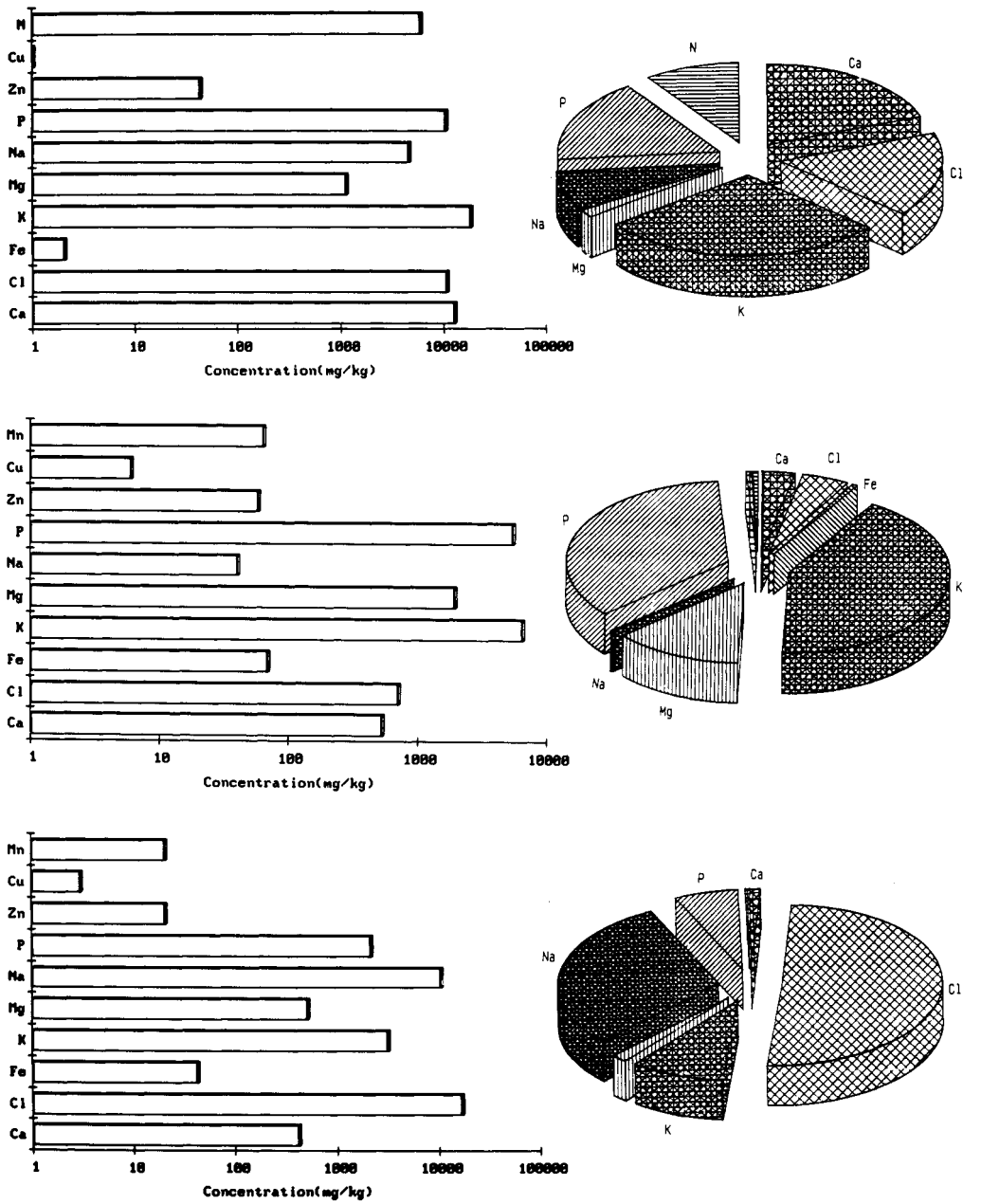

Fig. 5 a 63 skim milk powder b 189 whole meal flour c 191 brown bread

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