Talanta 131 (2015) 292–300

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Review

Total indices as a tool to estimate sum content of similar analytes

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ARTICLE INFO

Article history:
Received 28 May 2014
Received in revised form
28 July 2014
Accepted 31 July 2014
Available online 8 August 2014

Keywords:
Chemical analysis
Environmental analysis
Determination of organic substances
Sum content of similar analytes
Total indices
Standard substance
Uncertainty of results

ABSTRACT

The estimation of sum content of similar analytes without their separation often requires the use of total indices (TIs) expressed in terms of the standard substance concentration. Theoretic and metrological features of such indices are discussed in the review. The sum content of similar analytes is estimated by any TI with a certain systematic error. It can be minimized by selecting a standard substance and/or with the justification of sensitivity coefficients for individual analytes. The publications are pointed out in which new TIs are offered or new methods to measure known TIs are described. The corresponding studies are predominantly associated with two kinds of estimates: (a) total content of organic substances in waters and (b) the total antioxidant activity of foodstuffs.

Contents

1. Introduction

The problems which arise in the chemical analysis of unseparated mixtures, as well as the methods to solve these problems, do not depend so much on the mixture composition as on the task to be solved during the analysis. The general approach to the problem solution (with or without the components separation) is important too. The quantitative analysis of technologic or natural mixtures on the molecular level includes four main objectives [1]: (a) the determination of a certain component (X) in the presence of other components; (b) simultaneous and separate determination of several components (X_1, X_2, X_3,...); (c) determination of the total content of a number of components (usually similar ones) which form a certain group (ΣX); and

http://dx.doi.org/10.1016/j.talanta.2014.07.102
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(d) simultaneous and separate determination of several groups (ΣX, ΣY, $\Sigma Z\ldots$).

The problems of c-type are permanently solved in the analysis of waters, petroleum products, foodstuff and biological objects. The proportion of the relevant procedures in the general array of methods of chemical analysis is considered to constitute about 20% [2]. The rejection of separate determination of numerous similar substances accelerates, cheapens and simplifies the analysis of any object, and consumers still get the information they need. The ways to solve the problems of c-type and the allied but more complicated problems of d-type have been developed empirically since the 1930s. The corresponded techniques were often created not by professional analysts but by other specialists (engineers, hydrochemists, biochemists, etc.). In an analysts' opinion, the general theoretical problems arising from the evaluation of the total content (C_Σ) of similar substances without their separation are not studied enough [3–5]. The article of Valcarcel and Baena [2] had fundamental significance for the correct appreciation of these problems. After that the fruitful discussion of methods to estimate the sum content of similar analytes was started. Corresponding experiments were developed, especially in Russia [3]. Generalized approach [2] will be used in this review too, but it is worthwhile to limit the problem for discussion by quite narrow bounds. Namely, we are going to discuss the only kind of sum estimates- so-called *total indices* (TIs) expressed in terms of standard substance concentration. The examples can be the phenol index, hydrocarbon index, COD, antioxidant activity index, “total protein”, “total organic carbon”, etc. “Recalculated” TIs are usually determined by spectrometric methods (Fig. 1). Some titrimetric and electrochemical methods are used too.

TI-system has proved to be useful, but so far poorly substantiated in relation to metrology. The result of determination of TI (C^*) is often very different from C_Σ, sometimes several times as much [5]. Plausible reasons of corresponding errors and the ways to diminish them would be briefly examined in this review. We believe that the theoretical aspects of TI application are better considered in a general way, without singling out special groups of analytes or objects to analyze. The works in the field of analysis of natural and waste waters, petroleum products and foodstuff published since 2000 will be used as examples.

2. Methodology to determine the total content of similar analytes

2.1. Selection of the similar analytes

To determine any group of substances it is necessary to properly form the group content. It is recommended to use the following criteria for the selection of substances [2].

1) *Structural similarity of molecules*: proteins, alcohols, phenols, nucleic acids and others are singled out as certain groups of analytes. Such groups can be formed at different levels (hydrocarbons on the whole, aromatic hydrocarbons, polycyclic aromatic hydrocarbons, etc.). The group may include all the substances containing some element; their total content is recalculated to this element (“total carbon”, “total nitrogen,” etc.).
2) *Similar properties and similar application of the substances*: the compounds of different chemical nature may have similar properties (antioxidants, pesticides, etc.) which causes the need to evaluate their sum content. Sometimes groups of analytes are formed by taking into consideration both criteria simultaneously (polyphenol antioxidants, organophosphorous pesticides, cationic detergents).

Obviously, it is necessary to develop methods of sample preparation or signal measuring based on the desired composition of the group, and not vice versa. Unfortunately, groups of analytes are often formed, taking into account only the possibility of simultaneous extraction (adsorption, distillation, precipitation) or their simultaneous light absorption at a certain wavelength. This approach facilitates the elaboration of analytical methods, but the obtained results are difficult to interpret and apply. The data on group composition of objects of this type obtained by using different methods turn out to be incomparable! “Phenol index” (PI) widely applied in hydrochemical analysis can serve as a good example. PI characterizes the total content of volatile phenols which react with 4-aminoantipyrine in alkaline medium, recalculated to simplest phenol. However, certain substituted phenols (e.g. p-cresol) do not react with 4-aminoantipyrine and their content in a sample is not taken into account [6]. On the contrary, some non-phenolic components of the sample can react with 4-aminoantipyrine and make their contribution to the PI value. So the PI

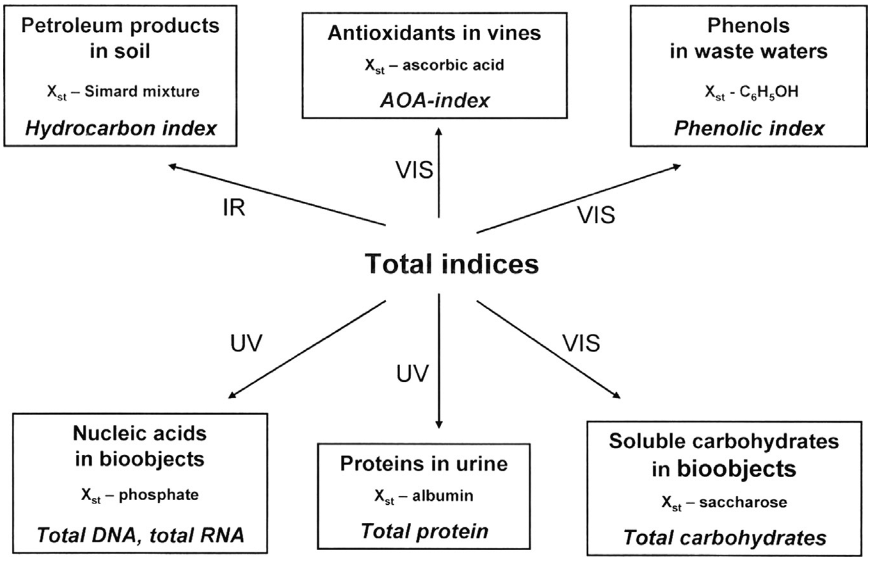

Fig. 1. The examples of total indices determined by UV, IR or visible (VIS) spectra.