NEW EQUATIONS DESCRIBING THE COMBINED EFFECT OF pH AND ORGANIC MODIFIER CONTENT ON THE RETENTION IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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Five new equations that express the combined effect of pH and organic modifier concentration in the mobile phase on the capacity factor in reversed phase liquid chromatography (RPLC) are developed based on either the adsorption or the partition model for retention. It is shown that a new seven-parameter equation is the best, since it exhibits good numerical behavior, does not predict physically meaningless retention surfaces and is the most accurate equation giving the lowest value of the sum of squares of residuals. In contrast, the conventional equations used up to now are less accurate and they may predict retention surfaces with physically meaningless portions. Finally, it is shown that the pK values of weak acids or bases can be determined chromatographically only if the ratio of the activity coefficients of the charged and uncharged eluted species is known from independent measurements. The fact that this ratio was not taken into account in relevant studies may explain the differences between chromatographic and potentiometric pK values found in literature.

THE CONNECTION BETWEEN TITANIUM CONTENT, BLEACHING AND FR PROTECTION OF WOOL

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Wool is a low flammable material (LOI 25.2). The wide use in the high risk environments needs FR treatment for better protection. The bleaching of wool is an actual process in the textile industry. In our earlier work, we find out that the degree of FR protection is in a direct correspondence with the quantity of connected Ti in the wool. The cystine oxidation by peroxide bleaching of the wool is resulting in cystine disulfide cleavage, partly. The FR treatment contributed to some changes in the wool fiber too. That’s is why we tried to explain what happened in the wool if these two procedures are used. So, the aim of this work was to find the connection between Ti content, bleaching and FR protection. For that propose we prepared two types of samples: FR treated only, and bleached and FR treated after that to the same conditions of FR treatment.

The appropriate used bleaching system of hydrogen peroxide and optical brightener Blankit enabled good degree of whiteness. The degree of FR protection for the both types of samples was investigated through the quantity of connected Ti, which was determined using UV-Vis spectroscopy.
These investigations showed us the next conclusions:

- Spectrophotometric method is a very convenient precise and fast for Ti determination
- The influence of bleaching is shown through the lower quantity of connected Ti in the bleached and FR treated samples in a comparison with the FR treated only.
- The breaking of S-S bonds during the bleaching resulting with a lower possibility of TiF$_2^-$ penetration in the wool.

METAL COMPLEX COMPOUNDS AS CHEMICAL MODIFIERS IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Key words: chemical modifiers, metal complex modifiers, ETAAS, thermal stabilization

The problem of detection limit decrease and improvement in accuracy of metal microimpurities determination in complex matrixes by ETAAS can be solved by the improvement of the equipment and by chemical modifiers allowing to change high-temperature processes of free atoms formation and to carry out controlled atomization. Metal complex chemical modifiers – chelates of metal ions with organic ligands (e. g. quinolinates, pyridylazoresorcinates, complexonates of Fe (III), Cu (II), Co (II), Ni (II), Mn(II), Mg (II) - combine advantages of organic and inorganic modifiers. The efficiency of all examined modifiers exceed considerably both efficiency of the respective inorganic complex-forming ion salts and organic ligand reagent. Their use save palladium salts while the same metrological characteristics of techniques are retained. At the choice of metal complex chemical modifiers it is necessary to take into account a mechanism of analyte free atoms formation in graphite furnace and a number of specific factors do not considered previously, such as influence of medium acidity; possibility of competitive reactions in a solution (I) and in a solid phase (s):

(i) \[ \text{MeL} + n\text{H}^+ = \text{Me}^{n+} + n\text{H}_2\text{L} \] (I), where L is organic ligand
(ii) \[ \text{Me}_{m}\text{L} + \text{Me}_{m}^{n+} = \text{Me}_{m}^{n+} + \text{Me}_{m}\text{L} \] (I, s)
(iii) \[ \text{MeL} + \text{H}_2\text{O} = \text{Me(OH)}\text{L} + \text{H}^+ \] (I)
(iv) \[ \text{Me}_{m}\text{L} + \text{Me}_{n} = \text{Me}_{m}\text{Me}_{n}\text{L} \] (I, s)

The study of metal complex compounds - quinolinates, pyridylazoresorcinates, and complexonates of metals - shows that efficiency of such modifiers depends on completeness of complex-forming ion binding into complex compound. Among copper and magnesium quinolinates Cu(Ox)$_2$ is more effective while its ability to react (ii) with Cd(II), In(III), Sb(III), Ni(II), Mn(II) ions is negligible. However, it cannot except a possibility of such reactions in the solid phase. Then, an abnormally high efficiency of magnesium quinolate for the indium determination is caused by solid-phase exchange reaction (ii). A similar relationship is established for metals complexonates. For example, germanium limit of detection decreasing coefficient in the presence of modifiers clearly correlate with value of stability constant of metal complex compounds. The success of metal complex modifiers application is determined by pH value. For instance, for the ETAAS germanium determination in the acidic medium stable complexonates FeEDTA' and BiEDTA' are more effective, while FeEDTA' hydrolyzes at pH=6 in accordance with (iii) and it is ineffective.

It is established that the main factor determining modifiers thermostabilizing is the nature of coordinated ligand. Metal complex modifiers accomplish analyte thermal stabilization at all