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Determination of Metal−Ligand Stoichiometries for Inorganic Complexes Using Total Reflection X-ray Fluorescence

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The methods usually used to determine the ratio metal−ligand in inorganic complexes require a set of solutions with different concentrations for both the ligand and metal. We propose a new method using the total reflection X-ray fluorescence technique, in which the ratio between metal and ligand is determined precisely, easily, and quickly. Experimental results provide evidence that for different chemical complexes, the ligand−metal ratio determined by this technique deviates at most from stoichiometric values by 6%. The technique is restricted usually to elements with Z above 14, and its detection limit is on the order of 10^{-8} g/g.

Introduction

The stoichiometric determination of the metal−ligand ratio is the first step in the characterization of a new complex and provides complementary information in studies to obtain information on its structure. Methods most often used are: Job's method[1,2] and polarographic techniques.[3] All these methods require a large set of solutions of different concentrations for both the ligand and the metal. This requirement may be an obstacle when expensive elements are involved. Moreover, the procedure to prepare the solutions, other than being time-consuming, is frequently accompanied by large errors in those cases in which the ligand or the metal is present in trace amounts.[4] To overcome these drawbacks and take advantage of advanced analytical techniques that are available today, we developed a new method using total reflection X-ray fluorescence (TXRF). TXRF is a relatively new technique that has been an efficient, fast method of elemental analysis[5] for both the quantitative and qualitative determination of elements with $Z > 14$. The method is advantageous because it is multielemental, has low detection limits (on the order of tens of nanograms per gram), and requires minute specimen quantities. Furthermore, the usual practice of adding an internal standard to affect quantification may often be avoided in the analysis of trace elements in organic matrix materials[6] because most of the constituent of the ligands are low Z elements. The applicability of TXRF is fully realized for metal−ligand ratio determinations when the ligand contains at least one atom that may be easily identified by the TXRF method, for instance, S, Cl, Br, and I, among others. When these elements are present in a sample, the metal−ligand molar ratio is determined by quantifying the metal and the element identified in the ligand. The method was developed to verify the stoichiometry of a sample of tin tributyl chloride, which was synthesized in our laboratory.

Theoretical Considerations. The basic equation for TXRF for a thin film is given by[7]:

$$I_i = K_i I_0 N_0 \sigma_i \omega_i m_i / A_i \tag{1}$$

where I_i is the intensity of the line from element *i*, K_i is a function of the measurement geometry and detection efficiency, I_o is the intensity of the excitation source. N_o is Avogadro's number; m_i is the areal density of the element with atomic number Z_i and atomic mass A_i. The collision cross-section for the element *i* is σ_i, and ω_i is the photon emission probability per ionization.

Because the solution does not deposit homogeneously on the reflector, changes in the value of $I_o m_i$ are produced, which results in significant variations of the total counts in different depositions of the same sample. To avoid this uncertainty, an internal standard is added to the solution in a well-defined concentration. It should be an element not originally present in the solution. In the data processing, the concentration of the original unknown elements are made in reference to the concentration of the added standard.

If a small amount of the element *j* is added to the original sample, the relationship between intensities becomes:

$$\frac{I_i}{I_j} = \frac{K_i \sigma_i \omega_i m_i A_j}{K_j \sigma_j \omega_j A_i} \tag{2}$$

Since the ratio m_i/m_j is the same as the ratio between the concentration of these elements in the solution (C_i/C_j), eq 2 can

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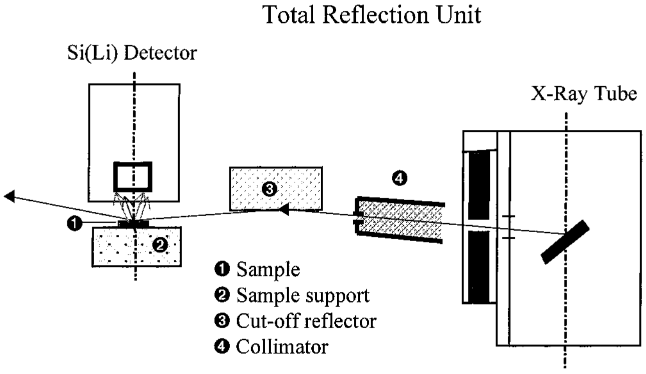

Figure 1. Experimental setup of the total reflection module.

be written[8]:

$$C_i = \frac{I_i S_i}{I_j S_j} C_j \tag{3}$$

where $S = K\sigma\omega/A$ is the relative sensitivity, either of the analyte element, i, or of the internal standard, j. It may be observed from eq 3 that, to determine the concentration C_i, the relative sensitivity calibration (S_j/S_i) must be a known value for a set of elements of analytical interest.

To perform the calibration, reference solutions are necessary. Each one of them must contain several elements with well-determined concentrations. Because an internal standard common to the solutions is required by this method, at least one element must be present in all the samples. From the spectral analysis point of view, it is possible to introduce any element as the internal standard in a particular standard solution. This is a feature of the software program SAX[9] used, which defines the relative sensitivity curve applying the following equation:

$$\frac{S_k}{S_i} = \frac{S_j/S_i}{S_j/S_k} \tag{4}$$

where the symbols used were already defined and k represents the element considered as the internal standard in the particular standard solution used.

Experimental Section

X-ray Spectrometer. The TXRF analytical system used in this study is a modified unit designed at the Atominstitut which is enclosed in a suitably designed X-ray biological shield. It consists of a high-voltage generator (Simens Kristaloflex 710 H), operated at 40 kV and 20 mA, which supplies a molybdenum anode X-ray tube (Philips model 2215/20) attached to the TXRF module.[10] The system includes a Si(Li) detector (Canberra SL 30180). The energy resolution of the detector is 180 eV for the Mn K_α line (5.9 keV). A schematic of the experimental set up is show in Figure 1. The spectrum was collected using a PC-based multichannel analyzer (Canberra model S100).

Data Analysis. The interpretation of the spectra and elemental quantification was performed by the X-ray analysis software program SAX.[8] X-ray spectra with energy ranging from 1.5 to 18.5 keV collected by the Camberra S100 MCA were converted to the SAX software format. SAX calculates the background by an iterative peak-stripping routine. Elements are identified in an interactive procedure contrasting operator experience with X-ray library suggestions. Then the signal intensities for each element are calculated by a least-squares fitting routine.

Table 1. Molar Ratio of Ligand to Metal Measured by TXRF for Several Compounds[a]

compounds	elements determined	molar ratio
CuCl	Cl/Cu	1.07 ± 0.03
$CuCl_2$	Cl/Cu	1.91 ± 0.03
K_2CrO_4	K/Cr	1.96 ± 0.04
$K_2Cr_2O_7$	K/Cr	0.92 ± 0.01
KBr	K/Br	1.07 ± 0.06
KCl	K/Cl	1.03 ± 0.06
$FeSO_4$	S/Fe	1.02 ± 0.03
$NH_4Fe(SO_4)_2$	S/Fe	2.04 ± 0.03
$C_7H_7ClNNaO_2S$	S/Cl	0.97 ± 0.05
$SnCl_2$	Cl/Sn	1.92 ± 0.07
n-Bu_3SnCl	Cl/Sn	0.94 ± 0.06
Vitamin B_{12}	P/Co	0.99 ± 0.01
$Cu(C_3H_5OS_2)_2$	S/Cu	3.93 ± 0.05

[a] Uncertainties are statistical counting errors.

Element concentrations in each specimen were derived from X-ray signal intensities by a TXRF quantification routine in SAX. It uses spectra of multielemental aqueous standard solutions prepared of elements with K-line or L-line X-ray emissions in the given energy range. The instrumental sensitivity relative to the chosen internal standard element is derived using eq 4. Finally, concentrations of elements were calculated from signal intensities using eq 3.

Sample Preparation. It is necessary to prepare a solution of the chemical complex with use of a solvent that may be dried by evaporation under vacuum or by the use of an IR lamp. A volume of 10 μL of the sample solutions under analysis was deposited with a micropipet on a 30-mm-diameter quartz reflector and dried by evaporation under low pressure (10^{-2} mbar). A set of 12 different compounds (see Table 1) were selected. None of the compounds presented particular handling hazards. Commercial reagents (Riedel de Haen) were used as supplied with the exception of the sample of tin tributil chloride used in this study.

For each compound an aqueous solution was prepared of which a volume of 10 μL was analyzed. An irradiation and data collection time of 1000 s was preset for all samples, and five measurements were performed for each one.

The sensitivity curve was obtained by analyzing six different standard solutions, two of them containing S, Cr, Ni, Co, Zn, As, Se, and Sr, with concentrations in the range of 10−20 ppm. The other four solutions contained K, V, Co, Zn, Se, and Sr with concentrations of 10, 30, 50, and 70 ppm of each element. Cobalt was selected as the internal standard. The instrument calibration curve is reported in Figure 2.

Results and Discussion

The set of samples analyzed and the experimentally obtained molar ratios are listed in Table 1. The quality of the analysis of the sample which was placed on the reflector is affected by: (1) The accuracy of the spectrometer sensitivity curve and (2) statistical counting errors.

To reduce these sources of error careful procedures were implemented and the molar ratios shown in Table 1 deviate at most from stoichiometric values by 6%. The accuracy of the spectrometer calibration is affected by possible errors in the elemental concentrations of the standards and also by statistical counting errors when the spectra of the standards are collected. For low Z, particular care must be taken because the decreased sensitivity for these elements. Statistical errors may also be reduced by increasing the X-ray irradiation intensity, by depositing larger sample volumes on the reflector, or by longer counting times.

The detection limits (DL) for the set of elements reported in this study are given in Table 2, and they reflect the variable

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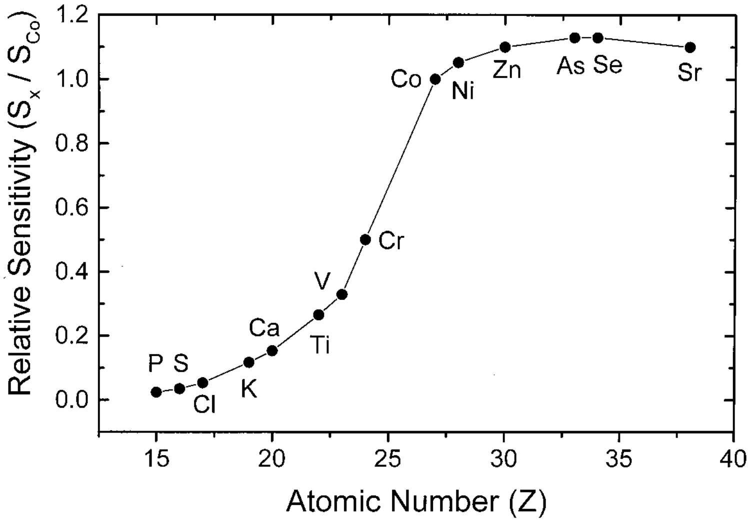

Figure 2. Relative sensitivity curve referenced to the cobalt concentration.

Table 2. Detection Limits for the Elements Considered in This Study

element	DL (μg/mL)
P	11.00
S	9.00
Cl	0.60
K	0.50
Cr	0.30
Cu	0.04
Fe	0.04
Br	0.05
Sn	0.16

sensitivity of the system. They were calculated by the use of[6]:

$$\mathrm{DL} = (C_i/I_i)*3*\sqrt{\mathrm{Bkgd}} \qquad (5)$$

where I_i is the total number of counts produced by the sample with element i of concentration C_i and Bkgd is the number of counts of the region of interest (ROI) due to the background.

Conclusion

The procedure developed to determine the metal−ligand ratio in organic complexes is simpler and faster than previously reported methods and provides adequate accuracy and detection limits. The method is particularly convenient when expensive or rare samples are available. It makes quantitative analysis of the metal−ligand ratio possible without the need of special standards of the elements being analyzed. The procedure is limited, in conventional TXRF, to the analysis of complexes containing at least one element with Z higher than 14. The range of elements can be increased by the use of a vitreous carbon sample support, a vacuum chamber, and a thin window or windowless Si(Li) detector. These modifications would allow the measurement with TXRF of oxygen and magnesium with predicted LLD of 108 and 23 ppm, respectively.[11]

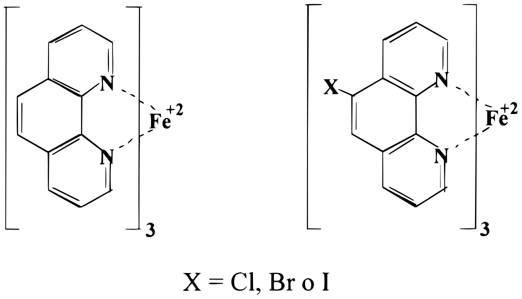

Figure 3. By introducing halogen atom X into the molecule on the left, the metal−ligand ratio may be determined in the molecule on the right by the method described in this article.

On the other hand, the limited number of complexes that can be determined with this technique may be overcome by introducing a halogen atom, X, into the molecular structure of the ligand. If this change in the complex structure does not modify it otherwise, the stoichiometric metal−ligand ratio may be determined by a measurement of the metal−halogen ratio. A typical example is given in the Figure 3.

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