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Species Determination of Organometallic Compounds Using Zeeman Atomic Absorption Spectroscopy with Liquid Chromatography

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Over the past several years we have devised and expanded the capabilities of Zeeman atomic absorption spectroscopy (ZAA).[1)-5)] Using this technique, trace elements in a complex matrix can be directly analyzed with high accuracy even when there is only one atom of interest contained in several million atoms of the host material. Quantities in the nanogram, or in some cases picogram, range can be determined within 15 seconds for more than 30 elements. Because of its high selectivity and high sensitivity, ZAA can be used as a new technique for organometallic species determination by interfacing with a high pressure liquid chromatograph (HPLC). The HPLC separates various molecular species. Different kinds of mobil solvents can be directly introduced in the ZAA detection system; even organic solvents or high concentration salt solutions. Then, organometallic species in the ppb range are separately detected according to their retention times. This technique has a much larger field of application than HPLC coupled with conventional AA[6)-8)].

The advantages of the ZAA technique are described in a recent publication.[5)] In this case, a steady magnetic field at 11 kgauss is applied to the sample vapor perpendicular to the incident light beam. The difference in absorption of the polarized constituents $P_{\perp}$ and $P_{//}$ is proportional to the atomic density, but is not affected by the various kind of spectral interferences caused by thermal decomposition of the eluants. The recently developed HPLC technique has many advantages over gas chromatography. Nonvolatile, polar, thermally unstable molecules or high molecular weight compounds can be separated.[9)] In the present system, the main requirement is that the solute be soluble in the mobile solvent.

A demonstration of the operation of this system is provided by the analysis of a mixture of vitamin B12 and $Co(No_3)_2$. As shown in Figure 1, vitamin B12 has a Co in its functional center.[10)] Sample 1 contained Co of 0.813 μg/ml

in the vitamin B12 (cyanocobalamine form*) and the Co of 25.0 μg/ml that was introduced as $Co(NO_3)_2$. Sample 2 contained only vitamin B12 at the same concentration as that in Sample 1. 0.5 ml of the sample was eluted with CH_3COONH_4 [2 M] through an anion exchange column** at a flow rate of 1.0 ml/min. and pressure of 20 kg/cm^2.

The separation between vitamin B12 and $Co(NO_3)_2$ was confirmed by using UV absorption and coulmetry[11] at the same time as shown in Figure 1. The upper and lower traces in Figure 1 show the signals from the coulometric detector and the UV absorption detector, respectively. The first peak in the lower trace shows the appearance of the vitamin B12 and the second peak in the upper trace of the $Co(NO_3)_2$. After separation, the mobile solvent was directly introduced into a ZAA spectrophotometer by utilizing an automatic injector to measure the concentration of Co with time. For Sample 1, two Co concentration peaks were observed at the retention times of the vitamin B12 and $Co(NO_3)_2$. For sample 2, only one peak corresponding to vitamin B12 was observed.

Next, fractions A, B, C, with retention times between 2-5, 5-8, 8-11 min., respectively, were collected for both Sample 1 and Sample 2. 10 μl from each fraction of 3 ml was introduced into the ZAA spectrophotometer and the concentration of Co was measured at the wavelength of 240.7 nm. Table 1 shows the concentration of Co in each fraction. The concentration of Co bound to vitamin B12 could be obtained without interference even through the coexisting inorganic Co concentration was 30 times larger than that of Co in vitamin B12.

From Fraction A of both Sample 1 and Sample 2, about 0.12 ppm of Co was detected. This result shows that about 90% of Co bound to vitamin B12 was recovered in this experiment. The Co of 0.007 ppm in Fraction B shows the background level of this system. From the Fraction C of Sample 1, a comparatively high

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**Hitachi Ion Exchange Resin No2611

concentration of Co (3.63 ppm) was detected. However, in the Fraction C of Sample 2, only 0.127 ppm of Co, which might be attributed to the contamination from the reagents and HPLC, was observed. From Table 1 we can safely conclude that the concentration of Co bound to the vitamin B12 molecule could be obtained without any interference with the comparatively high concentration coexisting inorganic Co. Also the concentration of the inorganic Co could be obtained separately from the Co in vitamin B12.

Species determinations by the present technique have application to the field of biochemistry because many enzymes and coenzymes have a metal atom in their functional center. This type of analysis is also important in the environmental field because the toxicity of a metal depends upon its chemical form.

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Figure Caption

Figure 1

Separation between vitamin B12 and $Co(NO_3)_2$, Sample 1 of Table 1, Upper trace: Coulometric detector, Lower trace, UV absorption detector (253.6 nm).

Table 1

Concentration of Co in Each Francion Determined by ZAA (ppm)

Fraction and its collected perios	A (2 - 5 min)	B (5 - 8 min)	C (8 - 11 min)
Sample 1 (vitamin B12 and $Co(NO_3)_2$	0.126	0.007	3.63
Sample 2 (viatmin B12)	0.120	0.007	0.127

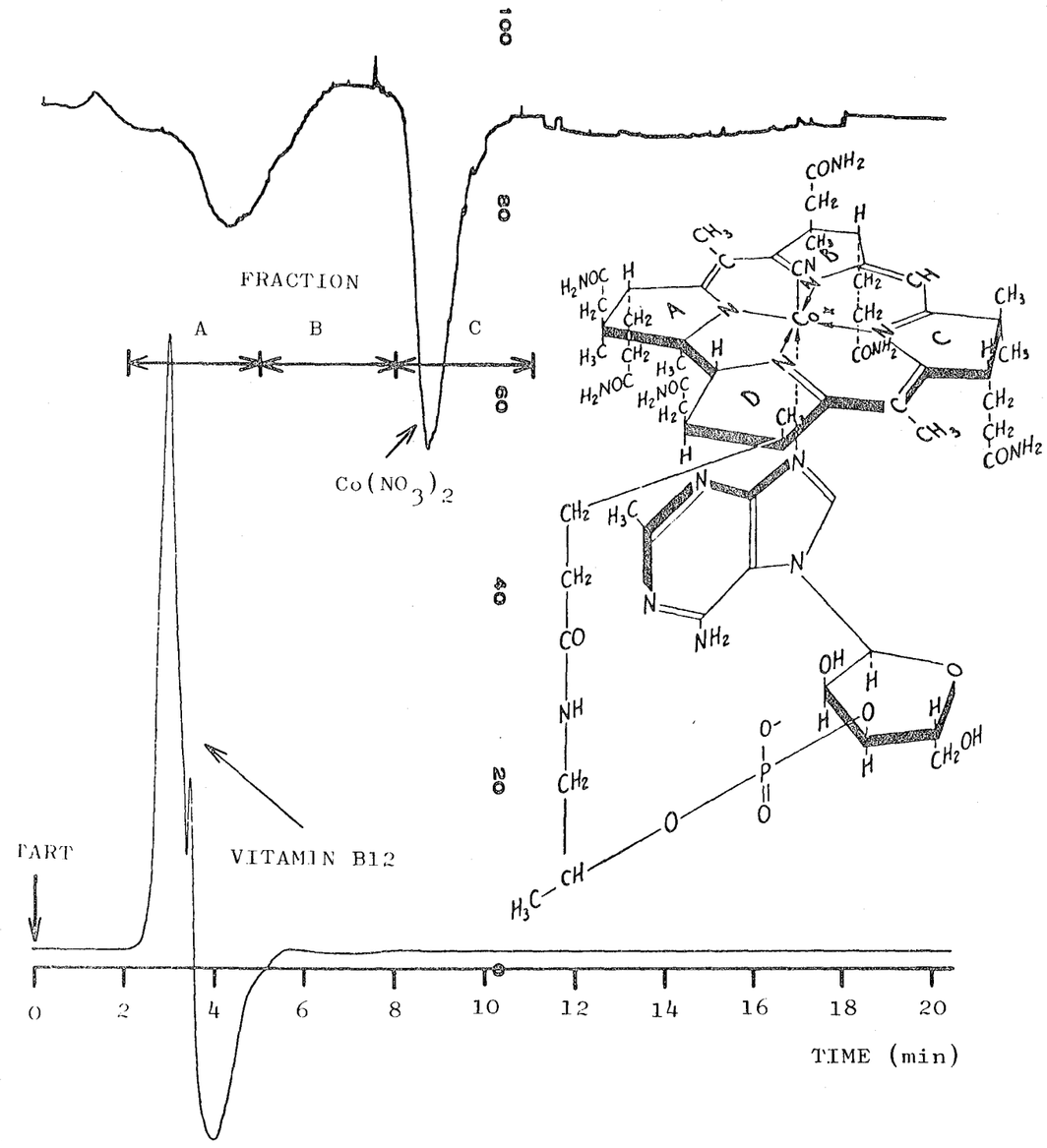

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Fig. 1

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