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Platinum-selective capillary gas chromatographic determination with microwave-induced plasma atomic emission detection

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Abstract

The volatile platinum(II) complex of *N,N*-ethylenebis(5,5-dimethyl-4-oxohexane-2-imine) (H_2APM_2en) eluted quantitatively from a GC capillary column and has been used to establish operating parameters and to gain figures of merit for atomic emission detection of platinum with microwave-induced plasma atomic emission. Two recipes have been developed for platinum; at 266 nm for simultaneous monitoring the carbon emission at 248 nm, and at 300 nm for simultaneous determinations with copper and nickel at 325 nm and 301 nm, respectively. Optimum platinum emission was observed using oxygen and hydrogen as reagent gases and high flow-rate of helium as make-up gas. Linear calibration ranges at 266 nm and 300 nm were assessed and, platinum emission being approximately five-times more sensitive at 300 nm than at 266 nm. The detection limit at 300 nm was observed as 65 pg/s. Selectivity of platinum emission over carbon at both wavelengths 266 nm and 300 nm is in the range of 10^5 – 10^6 . © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The major objectives of element-selective chromatographic detection are to obtain qualitative and quantitative determination of eluates, typically in interfering background matrixes, in terms of their elemental constitution.

Gas chromatography (GC) has been effectively coupled with atomic absorption spectroscopy, flame emission spectroscopy and noble gas plasma atomic

emission spectroscopy [1–5], the latter based primarily on the atmospheric pressure microwave-induced plasma (MIP) introduced by Beenakker [6] and commercialized with a water-cooled re-entrant cavity to maintain a helium plasma, modified as required by additional reagent gases [7,8]. The nitrogen purged spectrometer, based on a concave holographic grating, operates from 160 nm to 800 nm. The performance of this instrument has been extensively described for both non-metal- and metal-selective detection [9–19], although the most frequent applications in the latter area are for main group metals, particularly as sigma-bonded organometallics. Transition metal compounds have been less frequently evaluated, since stable volatile compounds, with the exception of 18 electron car-

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bonyls and metallocenes, are less frequently encountered.

Viable GC of transition metal chelates is determined by their volatility and thermal stability during injection and separation, tetradentate β -ketoamine ligands being of importance because of their selective quantitative reaction with various divalent metal ions [20,21]. Reagents of the family of *N,N'*-ethylenebis(4-oxopentane-2-imine), [bis-(acetylacetonate)-ethylenediimine, $H_2(enAA_2)$], incorporating various structural modifications to the alkylene bridge and/or the iminoketone functionality, have been applied widely for packed column [22,23] and capillary column GC separations. Copper and nickel [24], vanadium [25] and palladium complexes [26] have been chromatographed using atomic spectral detection. This paper describes the optimization and characterization of platinum-selective detection utilizing the platinum(II) chelate of *N,N'*-ethylenebis(5,5-dimethyl-4-oxohexane-2-imine) [bis-(acetyl-pivalylmethane)ethylenediimine] (H_2APM_2en) as a standard reference compound. This ligand has earlier proved useful for the GC determination of vanadium in crude oils at the 0.1 mg/g level [27]; it could in turn be applied to platinum determinations, for example in ore samples such as were analyzed for palladium by analogous ligands [28].

2. Experimental

The reagent H_2APM_2en and its copper(II), nickel(II) and palladium(II) complexes were prepared as reported elsewhere [22]. The platinum(II) complex was prepared by refluxing together the platinum(II) chloride-acetonitrile adduct and H_2APM_2en in benzene, following the general procedure of Belcher et al. [23]. Thermal stability and volatility of the complex was measured on a Shimadzu TG-30 thermal analyzer at a heating rate of 15°C/min and nitrogen flow-rate 50 ml/min. A Model 3700 gas chromatograph (Varian Instruments, Palo Alto, CA, USA) was used for flame ionization detection (FID). A Model HP 5890 II gas chromatograph (Hewlett-Packard, Avondale, PA, USA) was used with a manual and a HP 7673A autoinjector, and a split/splitless capillary injection port operated in the split mode; it was interfaced to a HP 5921

atomic emission detection (AED) system and HP 330 computer with HP 35920 GC-AED software. High-purity helium was used as carrier and make-up gas, and hydrogen and oxygen as reagent gases. The major features of the instrumentation are reported elsewhere [7,8].

Columns used were methylphenyl silicone fused-silica columns DB-5 (30 m \times 0.25 mm I.D. with 0.25 μ m layer film thickness) and DB-1 (4 m \times 0.32 mm I.D. with 0.17 μ m layer film thickness) (J&W Scientific, Folsom, CA, USA). Fresh solutions containing 1 mg/ml of complexes were prepared in acetone or cyclohexane and further solutions prepared by appropriate serial dilution.

3. Results and discussion

The ligand H_2APM_2en was chosen for platinum evaluation for both gas chromatographic and spectral detection reasons. The high thermal and thermodynamic stability of such tetradentate ligands ensures quantitative elution at the high column temperature needed. Although analogous and typically more volatile fluorinated chelates have been widely applied in GC, the possible changes in plasma discharge characteristics often observed in the presence of fluorine in analytes [29], suggest that definitive platinum quantitation is best performed in the absence of molecular fluorine. In mitigation for the reduction in volatility noted for non-fluorinated complexes in general, the presence of two tertiary butyl ligand substituents gives a notably more volatile species than occurs in their absence.

The stability of the platinum(II) complex is further indicated in the mass spectrum which shows a high-intensity molecular ion peak as base peak at m/z 501. Thermogravimetry in nitrogen with a 7.5 mg sample showed a loss in mass (volatilization) of >97% over a temperature range 230–340°C, with a maximum rate of loss at 310°C. This suggested that a short capillary column to be operated at a temperature of ca. 250°C would be most suitable.

The complex eluted as a single peak on a DB-5 (30 m \times 0.25 mm) column and was completely resolved from the copper, nickel and palladium chelates of the same ligand, H_2APM_2en (Fig. 1)

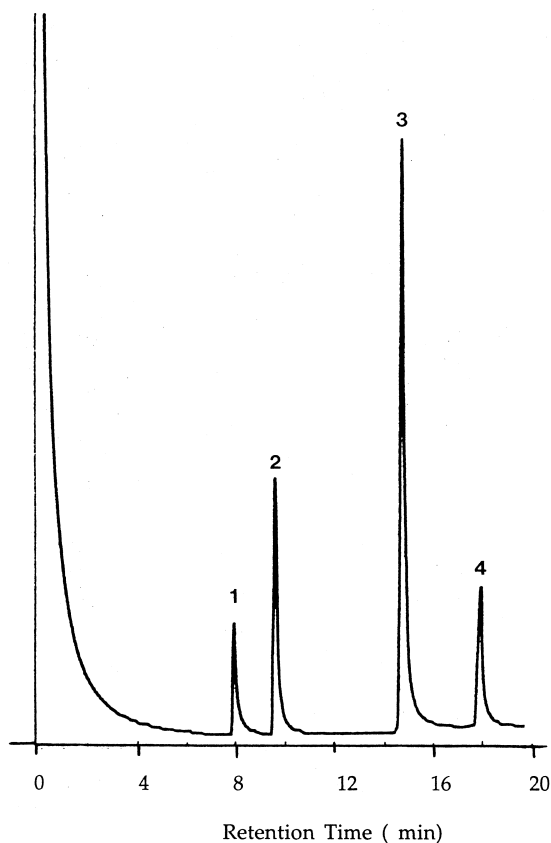


Fig. 1. Gas chromatographic separation of (1) copper, (2) nickel, (3) palladium and (4) platinum complexes of $H_2APM_2.en$. Column: DB5 (30 m \times 0.25 mm), column temperature 235°C for 12 min then programmed at 5°C/min to 250°C and isothermal for 10 min. Injection port and detector 260°C. Helium flow-rate 1.3 ml/min. Split ratio 1:20.

indicating it to be a suitable model candidate for the determination of operational parameters for the selective detection of platinum on the MIP-AED system.

The more intense emission lines referenced for platinum under inductively coupled plasma (ICP) [30] conditions were examined and those at 265.945 nm and 299.797 nm, which showed suitable responses, were selected for MIP-AED. The pixel signal “snapshots” indicated prominent signals at 265.991 nm and 299.837 nm (Fig. 2), clearly corresponding to the referenced lines. A three-dimensional display of snapshots (Fig. 3) shows the spectral

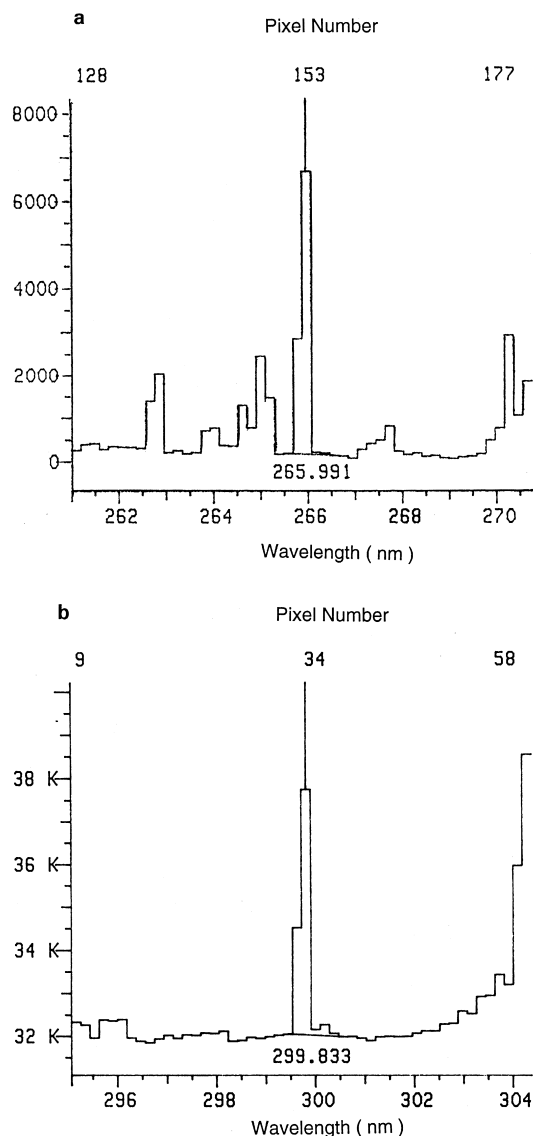


Fig. 2. Snapshot profiles of platinum (a) at 266 nm and (b) at 300 nm.

features of the emission of platinum, and reasonably symmetrical peaks are indicated.

A “recipe” is the set of parameters used in AED to detect one element. It consists of a software-based digital filter which provides continuous background correction for the desired response, as well as other parameters such as the location of the photodiode array on the spectrometer focal plane, the type of

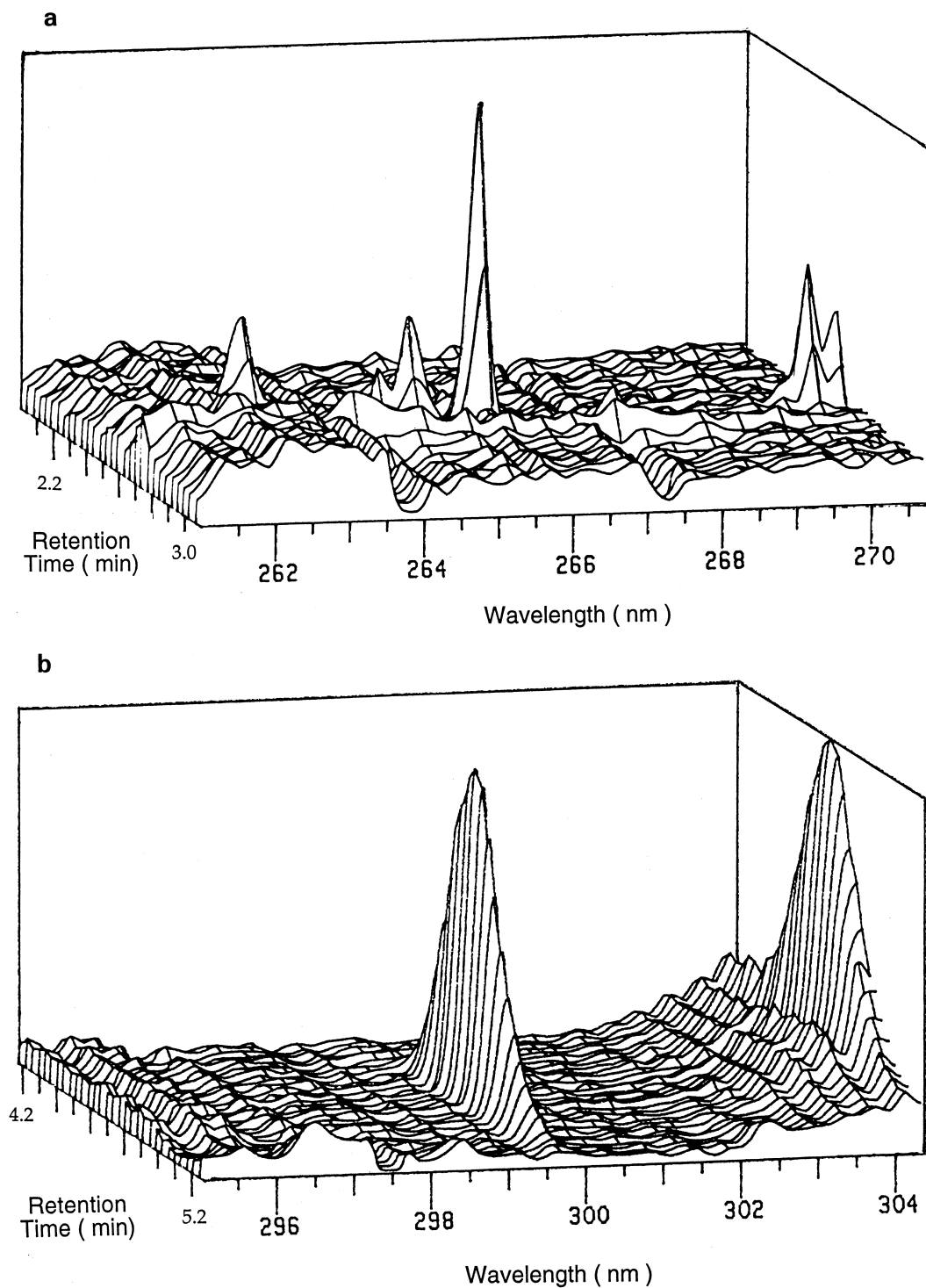


Fig. 3. Three-dimensional display of snapshots (a) at 266 nm and (b) at 300 nm.

reagent gases and the flow-rate of make-up plasma gas. No such recipe was previously available for platinum detection and these were thus developed by subtracting the continuous pixel background emission signal from the analyte signal as suggested by Sullivan and Quimby [8]. Once the spectral detection recipes were developed, the effect of make up gas (helium) and reagent gases (H_2 and O_2) on the emission lines were investigated. Platinum response was obtained using instrumentally set “high flow” make-up gas, hydrogen, oxygen or mixed hydrogen and oxygen as reagent gases. No response was obtained in the absence of reagent gases. Relatively poor sensitivity was observed using hydrogen only as reagent gas, better sensitivity using oxygen, but optimal sensitivity and good peak shape using hydrogen (0.03 ml/min) and oxygen (0.15 ml/min) together with helium make-up gas at 150 ml/min.

The platinum emission at 266 nm falls on the photodiode array detector within the window region for the carbon emission at 248 nm and these were recorded simultaneously for the complex. The carbon signal at 248 nm was stronger than for the platinum, in part because there are 18 carbon atoms as compared to one platinum in the molecule (Fig. 4). Similarly the platinum emission at 300 nm is within the region of nickel and copper at 301 nm and 325 nm, respectively, and thus was recorded from a mixture of copper(II), nickel(II) and platinum(II)

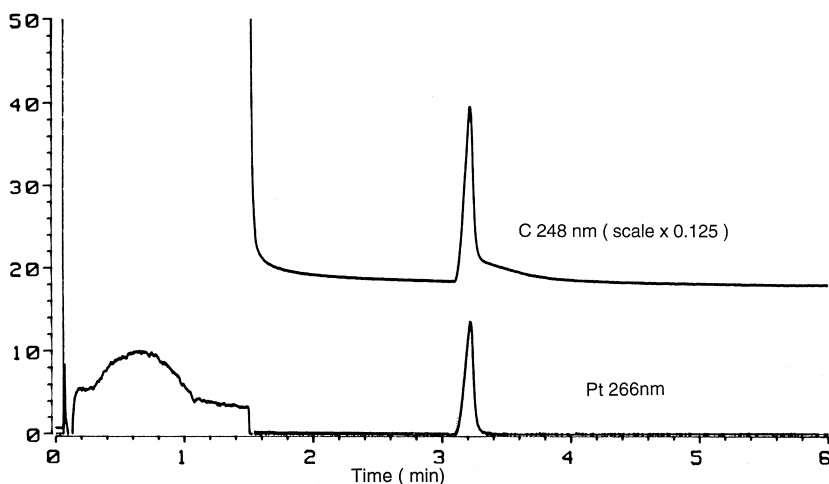


Fig. 4. MIP-AED response for the Pt(APM₂en) complex at Pt 266 nm and C 248 nm. Column: DB-1 (4 m×0.32 mm), column temperature 170°C programmed at 10°C/min to 210°C. Injection port 240°C. Helium flow-rate 11 ml/min. Split ratio 1:4.5.

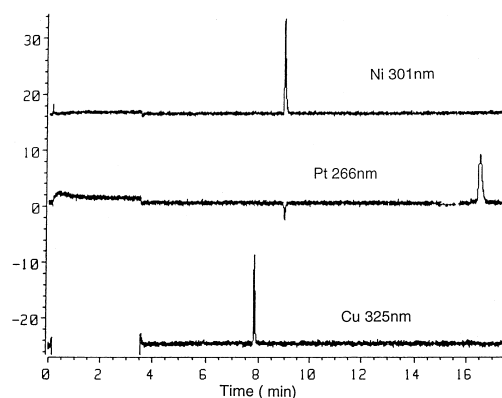


Fig. 5. Simultaneous chromatographic separation and MIP-AED detection of copper, nickel and platinum. Column as Fig. 1, column temperature 250°C injection temperature 260°C. Helium flow-rate 1.1 ml/min, split ratio 1:70.

complexes of ligand H_2APM_2en for possible simultaneous determination of copper, nickel and platinum (Fig. 5).

The selectivity of the platinum response at 266 nm and 300 nm against carbon was checked by adding octacosane ($C_{28}H_{58}$) to the platinum complex in molar ratio (100:1). The choice of a reference carbon compound which elutes in the same retention region as the analyte species is important in such measurements since selectivity must be determined in a linear response region of the chromatogram for each element. This criterion is typically not observed if

selectivity measurement is made against carbon response for a minimally retained solvent in which the analyte is dissolved. High selectivity of platinum emission over carbon emission at 266 nm and 300 nm was observed as $2.8 \cdot 10^5$ and $9 \cdot 10^5$, respectively. However, a small negative baseline excursion was sometimes observed for response at 266 nm as compared to 300 nm.

The linear dynamic range for platinum response was checked by injecting different amounts of complex and measuring average peak areas. Linear calibration curves at 266 nm and 300 nm were obtained up to ca. 250 ng of complex going to the detector, corresponding to ca. 100 ng platinum. Correlation coefficients of 0.99 and 0.98 were observed at 266 nm and 300 nm, respectively. It was observed that the AED sensitivity at 300 nm was five-times greater than at 266 nm. The detection limits measured at S/N of 3 were 320 pg/s and 65 pg/s platinum at 266 nm and 300 nm, respectively, indicating that the latter wavelength was preferred overall for platinum detection.

4. Conclusions

The overall analytical figures of merit for platinum specific detection by GC–MIP–AED suggest that this procedure is viable for volatilizable platinum compounds which also exhibit gas chromatographic integrity. The elemental detection limits obtained are dependent upon emission intensities of the atomic lines available for determination, their choice being also predicated by the desirability for minimal spectral interferences from the plasma background or other elements present in the analyte. Transition metal detection limits vary over a considerable range from iron at 0.3 pg/s to tungsten at ca. 50 pg/s [31]. However most such determinations were not made under the conditions applying to the present diode array system. Platinum does not fall into the most sensitive elemental category, but this is counteracted by the extremely high selectivity measured against carbon and good linear dynamic range. The latter factor is the more important in practical determinations, since sample loading can typically be increased for trace determinations provided that they are interference free. Application to platinum de-

rivatization and determinations, for example in ore samples, appears worthy of investigation [28]. In the realm of biotransformations of platinum drugs such as cisplatin, total element determinations or potentially molecular speciation of platinum would be of importance, as already evidenced in high-performance liquid chromatography (HPLC)–ICP–MS studies [32].

An important caveat still holds however for platinum as for other elements regarding compound independent calibration. Insufficient data are as yet available for wide ranges of compounds classes for many elements, particularly metals, to determine whether elemental response is truly independent of molecular bonding and functionality. As noted earlier, such independence is problematic for fluorine containing compounds and indications are that it may fail even for structurally similar compounds of transition metals such as iron [33]. In general the chromatographer is advised to follow standard analytical procedures for elemental quantitation in GC–AED by using external calibration or standard addition methods which work effectively.

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