

Development of a high-temperature gas chromatography–inductively coupled plasma mass spectrometry interface for the determination of metalloporphyrins

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ABSTRACT

The development of a high-temperature gas chromatography–inductively coupled plasma mass spectrometry interface is reported. The method is applied to the analysis of synthetic and geological metalloporphyrins and detection limits and retention indices are given.

INTRODUCTION

Metallated porphyrins (geoporphyrins) are common, and sometimes abundant, constituents of many crude oils, oil shales, coals and sedimentary rocks [1] and they have been proposed as useful maturity indicators in such substrates [2,3]. Geoporphyrins have also been shown to be important in an industrial context where they effect catalytic upgrading of crude oils by reducing catalyst lifetime or by catalysing the formation of unwanted byproducts [4]. The development of methods suitable for analysis of geoporphyrins is therefore an important goal for geochemists and petroleum chemists.

Most studies of geoporphyrins have focused on structural elucidation of the demetallated porphyrin macrocycle [5]. However, recent developments in high-performance liquid chromatography (HPLC) and gas chromatography (GC) have led to a number of reports of the metallated

species in geochemical samples [6,7]. This has the advantage that the selective decompositions which are observed during demetallation are avoided [8]. In addition, the study of intact metallospecies may extend reports beyond the common nickel and vanadyl compounds, leading to increased geochemical information. Notable amongst more recent reports is that of Boreham [8] who described high-resolution reversed-phase HPLC of nickel and vanadyl geoporphyrins in marine rocks from the Toolebuc Formation, Australia. An impressive resolution of the major classes of metalloporphyrin macrocycles was obtained but the detection method used (UV–Vis spectrophotometry) was not designed to provide information about metals other than nickel or vanadium. In contrast, the use of inductively coupled plasma (ICP) mass spectrometry (MS) as a metal-selective detector in our recent studies of metalloporphyrins in coals allowed us to demonstrate the distribution of gallium porphyrins but no detailed study of the macrocycle was possible [9].

GC separation of metalloporphyrins has at-

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tracted attention for a considerable time [10,11]. However, the advent of so-called high-temperature gas chromatography (HTGC) columns has seen some impressive advances. Thus, Blum and co-workers [12,13] were able to demonstrate the distributions of nickel and vanadyl porphyrins in Julia Creek and Serpiano oil shales by GC–flame ionization detection (FID) and GC–MS [electron impact and ammonia chemical ionization (CI)]. The latter has the advantage of providing both structural information as well as confirmation of the metal content. However modern GC–MS systems are not well-suited to the use of HTGC columns and aggressive CI reagent gases [13] and, to our knowledge no detection limits or quantitative analyses have been reported.

In the present report we describe the modification of a recently described GC–ICP–MS [14] system to allow quantitative determination of synthetic nickel, vanadyl, manganese, iron, copper and zinc metalloporphyrins and metalloporphyrins in samples of coals and oil shale. “Working limits” for quantitation are given and the practical retention range of organometallic compounds has been greatly extended. The method has considerable potential for the rapid metal profiling of geoporphyryns.

EXPERIMENTAL

Gas chromatography

A Carlo Erba HRGC 5300 Mega Series gas chromatograph equipped with a constant-pressure, constant-flow unit (Fisons, UK) was used. A 10 m × 0.32 mm, HT-5 (0.1 μm film thickness) aluminium clad high-temperature column (S.G.E., UK), with a helium (high purity, Air Products, UK) flow-rate of 3 cm³ min⁻¹ was used. Typical the temperature programme was from 60 to 410°C at 15 or 20°C min⁻¹ with a 5–10-min isothermal hold.

Inductively coupled plasma mass spectrometry

A VG Plasmaquad 2 (VG Elemental, UK) instrument was used under the operating conditions given in Table I. Commercially available software (VG Elemental) was used for data acquisition and a BASIC programme was used

TABLE I
ICP–MS OPERATING CONDITIONS

Cooling gas	15 l min ⁻¹
Auxiliary gas	1.0 l min ⁻¹
Injector gas	1.33 l min ⁻¹
Forward power	1500 W
Reflected power	<5 W
Mode	Time resolved analysis
Dwell time	Typically 1280 μs
No. of scans	Typically < 900
Data acquisition time	Typically < 10 min

for data processing and conversion. The ICP–MS system was tuned using a continuous cold vapour ²⁰²Hg signal [15].

Reagents

Synthetic metalloporphyrins. Synthetic nickel octaethylporphyrin (OEP), iron OEP chloride, vanadyl OEP, copper OEP, zinc OEP chloride and manganese OEP chloride were obtained from Aldrich, UK. Solutions were prepared in dichloromethane (Rathburn, UK) and examined on the same day.

Geoporphyryn samples. Bagworth coal was obtained from the British Coal Bank (Stoke Orchard, UK). The iron porphyrins were isolated as the chloride complexes using TLC [16]. Green River Shale was extracted (Soxhlet, 24 h) and porphyrins separated by flash column chromatography [17]. Nickel and vanadyl porphyrins were isolated by column chromatography. A Marl Slate nickel porphyrin fraction was obtained from Dr. A.J.G. Barwise (BP Research Centre, Sunbury-on-Thames, UK).

RESULTS AND DISCUSSION

Development of the HTGC–ICP–MS interface

The construction of the GC–ICP–MS interface and its application to the analysis of low- and medium-molecular-mass organometallic compounds has been described recently [14,15]. The GC retention index of the most retained analyte was ca. 3400 [15]. Metalloporphyrins typically have retention indices of ca. 5000 [18]. Thus, modification of the published interface was

needed before metalloporphyrins could be examined. The limitation of the GC–ICP–MS method to *ca.* 3400 retention index was thought to be due to the cooling effects of the argon injector gas (typical flow-rates 1.4–1.5 l min⁻¹).

Modifications of the GC–ICP–MS interface were made as shown in Fig. 1, which shows three major components; an argon heater, the heated transfer line and the demountable torch. The modifications to the ICP–MS system itself have already been described [14]. The main problem associated with heating argon is its low heat capacity. Therefore aggressive heating was needed and all tubing between the argon heater and ICP–MS injector insert was reduced to a minimum.

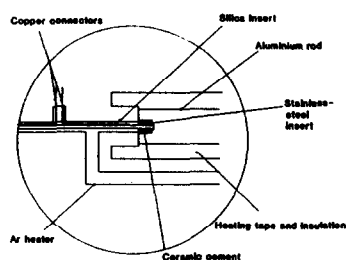
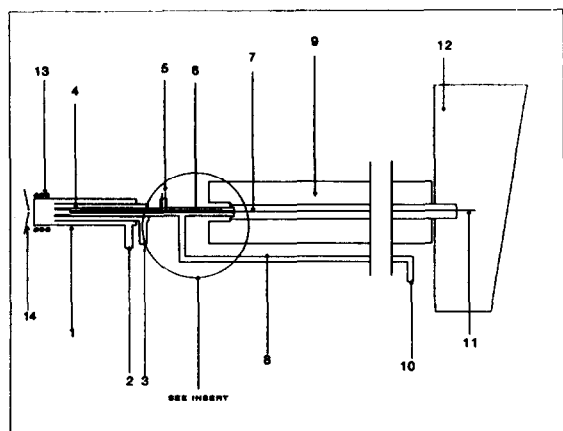


Fig. 1. HTGC–ICP–MS interface design. 1 = Plasma demountable torch; 2 = cooling gas inlet; 3 = auxiliary gas inlet; 4 = stainless-steel inset; 5 = outlet for copper leads (sealed with ceramic paste); 6 = copper wire leads; 7 = aluminium rod; 8 = argon heater; 9 = insulation; 10 = injector gas inlet; 11 = capillary column; 12 = GC oven; 13 = RF load coil; 14 = ICP–MS interface.

The argon heater consisted of nichrome wire inside a silica tube. The nichrome wire was heated to red heat with a suitable power supply (power requirement *ca.* 200 W) and the argon injector gas passed through the silica tube. The heater was insulated with Dalfratex cord (Darchem, UK) and further insulation was provided by industrial pipe lagging (Encon, UK).

The transfer line consisted of an aluminum rod through which the capillary column was threaded [14]. The transfer line and argon heater were grounded to the torch box.

A demountable torch with a 3 mm ICP injector insert (Baumbach and Co., UK) was used. A stainless-steel tube (1 mm × 12 mm) was mounted concentrically in the injector insert. The stainless-steel insert was introduced into a 2.5-mm hole in the aluminium rod. This not only provided support for the GC column, but ensured that the temperature was maintained above 400°C along the entire cross-section of the tube. The stainless-steel tube was resistively heated using a laboratory-made low-voltage power supply (power requirement *ca.* 150 W).

The GC column could only be extended to the end of the stainless-steel tube (24 mm from plasma), resulting in a dead volume of 0.70 cm³. Extending the capillary further (within 2 mm of plasma) resulted in a lower sensitivity and poor peak shape. Further extension of the stainless-steel tube would probably result in arcing from the RF load coil and was not attempted.

Evaluation of HTGC–ICP–MS interface

Fig. 2 shows a chromatogram obtained from HTGC–ICP–MS of five synthetic metalloporphyrins using the modified interface described above. The components eluted within a reasonable time (*ca.* 15–20 min) and had acceptable peak shapes. Furthermore, the specificity of ICP–MS as, effectively, a multielement chromatographic detection method, allowed all five metals to be monitored virtually simultaneously by selected ion recording (SIR; Fig. 2). The loss in resolution when comparing the HTGC–ICP–MS system to HTGC–FID was <1% (calculated on peak base width).

The detection limits for these porphyrins, and the estimated detection limit for vanadyl oc-

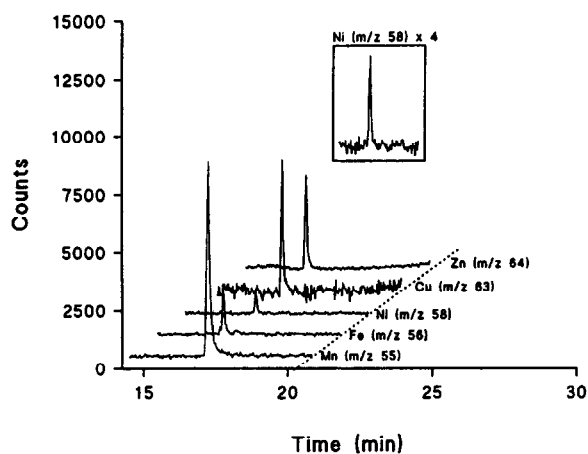


Fig. 2. Selected ion recording chromatograms of m/z 55 (Mn), m/z 56 (Fe), m/z 58 (Ni), m/z 63 (Cu) and m/z 64 (Zn). GC programme 60 to 350°C at 20°C min⁻¹, 350 to 410°C at 12°C min⁻¹, 1-min isothermal hold.

taethylporphyrin, are shown in Table II. These detection limits are “working limits”, calculated using temperature programmes that would normally be employed for geoporphyrin analyses. The method of tuning with ²⁰²Hg is not optimum. Alternative methods are currently being investigated and these may lead to improved limits.

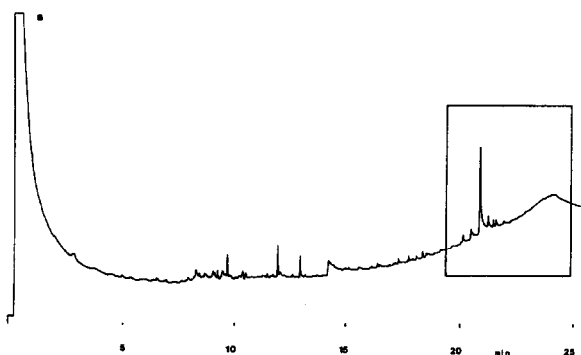


TABLE II

DETECTION LIMITS FOR SYNTHETIC METALLOPORPHYRINS

Metalloporphyrin	Retention index ^a	Detection limits ^b (ng on column)
Vanadyl OEP	6280	0.51
Manganese OEP Cl	6022	0.10
Iron OEP Cl	6213	0.30
Nickel OEP	6266	0.51
Copper OEP	6692	0.55
Zinc OEP Cl	6114	0.14

^a Calculated from *n*-alkane standards.

^b Calculated at 3 σ .

Analysis of geoporphyrins

Figs. 3–5 show HTGC–FID and HTGC–ICP–MS chromatograms of porphyrin-containing extracts from coal and oil shales. These figures clearly illustrate the specificity of the HTGC–ICP–MS method over HTGC–FID and show a considerable simplification of the chromatograms by SIR. For example, Fig. 3b shows selected ion HTGC–ICP–MS chromatograms of the porphyrin fraction isolated from the Green River Shale. The chromatographic peak shape of the vanadyl species is quite poor, whilst that of the

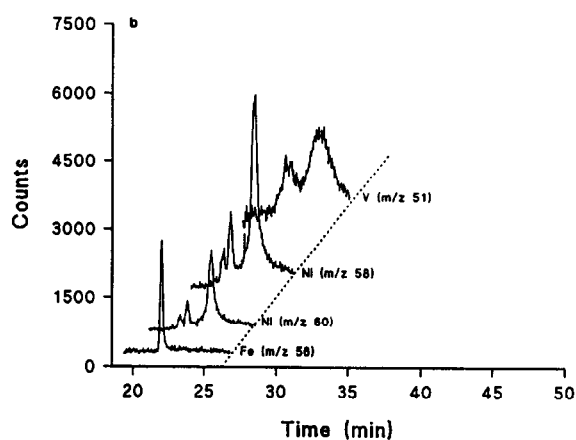


Fig. 3. (a) HTGC–FID chromatogram of Green River Shale porphyrin fraction, GC programme 60 to 410°C at 15°C min⁻¹, followed by an isothermal hold. Box indicates HTGC–ICP–MS chromatogram range. (b) HTGC–ICP–MS chromatogram (m/z 51, 56, 58, 60) of Green River Shale porphyrin fraction, GC programme 60 to 350°C at 15°C min⁻¹, 350°C at 10°C min⁻¹, 1.5 min-isothermal hold.

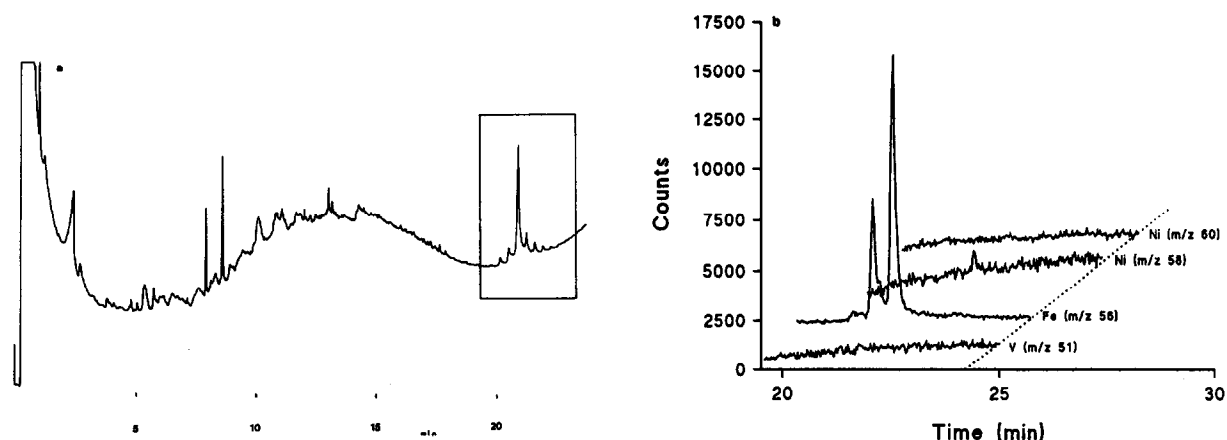


Fig. 4. (a) HTGC-FID chromatogram of iron porphyrin fraction from Bagworth coal, GC programme 60 to 410°C at 15°C min⁻¹, followed by an isothermal hold. Box indicates HTGC-ICP-MS chromatogram range. (b) HTGC-ICP-MS chromatogram (*m/z* 51, 56, 58, 60) of iron porphyrin fraction extracted from Bagworth coal, GC programme 60 to 350°C at 15°C min⁻¹, 350°C at 10°C min⁻¹.

nickel species is acceptable. Both nickel and vanadyl species could be quantified by reference to the added synthetic iron porphyrin internal standard (10 ng as iron).

The iron porphyrins isolated from a “standard” UK coal (Bagworth) [16] were also monitored by SIR (*m/z* 56) (Fig. 4b). The gallium porphyrins of this coal have been the subject of previous studies including HPLC-ICP-MS analysis [9], but to our knowledge this is the first

instrumental chromatographic technique applied to iron porphyrins in a coal. The only previous report of a chromatographic technique being applied to these porphyrins, used TLC [16].

Analysis of the so-called “nickel” porphyrin fraction from the Marl Slate by HTGC-ICP-MS (Fig. 5b) also revealed the presence of titanium porphyrins which co-elute with the nickel compounds but which could easily be distinguished by SIR (*m/z* 48). The close similarity in chro-

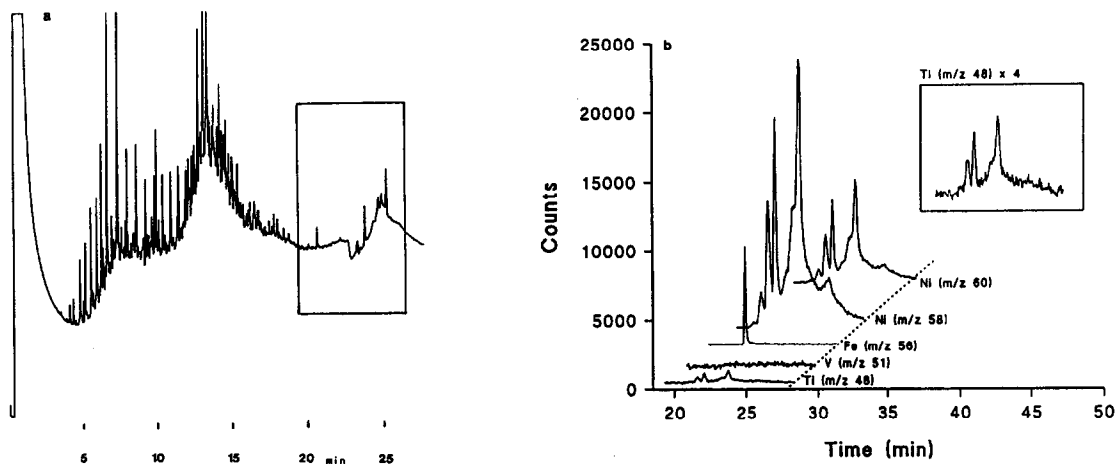


Fig. 5. (a) HTGC-FID chromatogram of Marl Slate nickel porphyrin fraction, GC programme 60 to 410°C at 15°C min⁻¹, followed by an isothermal hold. Box indicates HTGC-ICP-MS chromatogram range. (b) HTGC-ICP-MS chromatogram (*m/z* 48, 51, 56, 58, 60) of Marl Slate nickel porphyrin fraction, GC programme 60 to 350°C at 15°C min⁻¹, 350°C at 10°C min⁻¹, 2.8-min isothermal hold.

matographic behaviour of the nickel and titanium porphyrins possibly explains the lack of previous reports since less selective detection methods would not reveal their presence.

Titanium porphyrins have not been reported in geological samples previously, although Chicarelli *et al.* [17] speculated on their presence in several shales on the basis of off-line liquid chromatography followed by direct nebulization ICP-MS. Mango [19] commented on the catalytic activity of transition metals in catalysing reactions under conditions of diagenesis and mentioned titanium as one of the possible transition metal catalysts. Other workers have suggested that the poisoning of coal liquefaction catalysts was due in part to the presence of titanium porphyrins [20].

The gas chromatograms obtained for all of the geological porphyrin distributions were quite simple, as expected from previous studies [12,13,21,22]. This contrasts with the complexity revealed by HPLC methods [9] and reflects the greater resolving power of HPLC where variations in mobile phase and stationary phases allow separations to be maximized [5,6]. Hence the improved HPLC resolution of geoporphyrins mixtures over the last 12 years [8,23]. Whilst the lack of GC resolution is a disadvantage, the simplicity of the metal ion chromatograms does allow rapid metal profiles of geoporphyrins to be obtained and compared, and this is potentially valuable for screening source rocks or oils in petroleum exploration, petroleum refining or even oil pollution studies (*e.g.* tarball fingerprinting [24]).

The simple nature of the high-temperature gas chromatograms which typically consist of two or three peaks, may reflect the distributions of the major macrocycle types (*e.g.* deoxophyllerythroetioporphyrins and etioporphyrins) but this remains to be tested by coinjection of pure metalloporphyrins.

CONCLUSIONS

HTGC-ICP-MS is a selective and sensitive method for the rapid profiling of metalloporphyrins in geological samples. The method should find wide application in petroleum explo-

ration geochemistry, industrial petroleum refining and oil pollution studies.

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