ELEMENT-SELECTIVE GAS CHROMATOGRAPHIC DETECTION BY ATOMIC PLASMA EMISSION SPECTROSCOPY

REVIEW AND DEVELOPMENTS

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SUMMARY

The recent progress and current developments in element-specific detection for gas chromatography by atomic plasma emission spectroscopy are reviewed with emphasis on the applications of microwave-induced plasmas (MIPs) in capillary separations. A number of current applications of atmospheric-pressure MIP detection are then considered, including empirical formula measurement of cyclosiloxane pyrolyzates from silicones, ligand-exchange reactions of aluminum chelates, selectivity and sensitivity considerations in rhodium-specific detection, and dual-element detection for boron and iron in ferroceneboronate derivatives of diols.

INTRODUCTION

Chromatographic detectors may be "universal", "selective", or "specific". Detection of all eluted peaks is desirable for some applications, but it is often necessary to discriminate specific components in an incompletely resolved chromatogram or to carry out the analysis of one particular analyte class. Detectors may be "element-selective", "structure- or functionality-selective", or "property-selective". Specific detectors are those exhibiting a sufficiently high amount of selectivity to be effectively "blind" to eluates other than the target analyte. The separating capability of the chromatographic column can thus be complemented by selective detection to achieve enhanced analytical resolution.

The objectives of element-selective chromatographic detection are qualitative and quantitative measurement and identification of eluates, based upon elemental content; simultaneous multi-element detection may enable empirical formulae of eluates to be determined. Some element-selective detection methods are in common use in gas chromatography (GC): alkali flame ionization detection (AFID) often known as nitrogen–phosphorus detection (NPD), flame photometric detection (FPD), which is selective for sulfur and phosphorus, and Hall electrolytic conductivity detection (HECD), which is selective for halogens, nitrogen, or sulfur. In high-performance liquid chromatography (HPLC), element-selective detectors have been

little used. Atomic emission spectroscopy is a powerful method for such interfaced detection because of its capacity to monitor all elements; much recent effort has focused on its employment for on-line chromatographic detection. Various modes of atomic spectroscopy have been interfaced for GC detection, atomic absorption (AAS), flame emission (FES) atomic fluorescence (AFS) and atomic plasma emission. All these methods have also been used in HPLC detection. The scope of that work is summarized in a recent review[1].

THEORY

Survey of plasma emission GC detection

Inert gas plasma emission methods have strong analytical capability. Although sophisticated spectroscopic instrumentation is needed for simultaneous multi-element detection, sequential single-element detection can be achieved quite simply. Various atom reservoirs were developed to produce emission spectra from atoms rather than molecules, thereby enhancing detection selectivity. Complete molecular fragmentation also allows element rationing and empirical formula measurement[2]. The major plasma sources used in GC detection have been the microwave-induced helium plasma, at atmospheric or reduced pressure, the direct current argon plasma (DCP) and to a lesser extent the inductively coupled argon plasma (ICP). The microwave-induced plasma (MIP) system is the most economical to operate with respect to plasma gas usage and power requirements. The advantages of plasma emission detection include the ability to "speciate" for many metals and non-metals, either directly or by derivatization through suitable chemical reactions. (The term speciate involves determination of the specific molecular species in which the analyte elements occur.) There is also the ability to tolerate non-ideal chromatographic elution, to achieve high elemental sensitivity and carry out multi-element monitoring.

The major atom reservoirs used for GC detection have been microwave-indiced electrical discharges (plasmas). An argon or helium plasma is maintained within a microwave cavity, which focuses coupled power from a microwave source, usually operated at 2.45 GHz, into a sample discharge cell. The spectral emission is focused onto the entrance slit of a spectrometer; the detection system may consist of a photomultiplier tube, a number of tubes in the case of polychromators, or increasingly, diode arrays. The most frequently used plasma cavity for GC has been an atmospheric pressure device, sustained in a TM_{010} cavity of the type first described by Beenakker[3]. Other frequently used plasma sources have been reduced pressure cavities of the type introduced by Fehsenfeld *et al.*[4], which can also be used at atmospheric pressure for an argon plasma gas. The efficiency of the MIP also depends on waveguides, metal tubes which transfer power from a microwave generator to the plasma gas. If the waveguide configuration is "interrupted" to give total reflection of energy traveling along it, "standing waves" are set up to produce a "resonant cavity". A comparison of cavities for GC detection was made by Risby and Talmi[5]. Bache and Lisk[6] were among the first to employ a plasma detector to determine ng levels of Br, Cl, I, P and S in organic eluates. The reduced-pressure GC–MIP system was shown effective for P, S, Br, Cl, I, C, H, D, N, O and other elements by McLean *et al.*[7].

Line emission is observed for almost all elements in the helium plasma, giving an advantage for selective detection over the less-energetic argon MIP, in which such

elements as Cl, Br, N and O give weak diatomic molecular emission. GC detection limits were found in the 0.03–0.09 ng/s range[7], but the best selectivities against carbon were around 2000:1. This instrumental system was the precursor of commercial GC–MIP instrumentation[8] for which Brenner[9] evaluated the sensitivity, selectivity and reproducibility. Kewei et al.[10] have used a similar polychromator instrument for oxygen-specific detection; purified plasma gases and air exclusion from the system helped to optimize the detection limit at 0.3 ng/s.

Hagen et al.[11] used chlorodifluoroacetic anhydride derivatization to introduce element taggants F and Cl into amines to obtain improved GC–MIP selectivity and sensitivity. Olsen et al.[12] compared reduced-pressure and atmospheric-pressure MIP for detection of organomercury, selenium and arsenic. They found the latter system better, giving 1-pg detection for mercury with selectivity over carbon of 10 000. Quimby and Sullivan[13] described a cooled modified Beenakker cavity with exit-gas purge, a moveable diode array and a holographic concave grating for sensitive multi-element monitoring.

The applications of MIP in GC detection have been extended recently in various ways. Pivonka et al.[14] used a 370-W water-cooled Beenakker MIP system and a tangetial-flow torch[15] to gather time-resolved interferograms with a Fourier Transform near-infrared (FT-NIR) emission spectrometer. Computer-generated element specific chromatogram reconstructions for C, H, N, O, F, Cl, Br and S were obtained. The "surfatron" MIP cavity has been usefully applied for GC detection. Takigawa et al.[16] constructed a versatile multi-element detector by combining it with a photodiode-array spectrometer to give an isometric spectrochromatographic display of data. Rivière et al.[17] used a surfatron monochromator system to obtain low pg/s detection for Cl, P and S in pesticides. The surfatron has also proven viable as a detector for supercritical-fluid chromatography (SFC), affording sulfur-specific detection at the 25-pg/s limit for thiophene[18]. Extensive spectral characterization was carried out for this system for two common SFC mobile phases, carbon dioxide and nitrous oxide[19]. Helium afterglow[20] and radiofrequency plasma discharge detectors[21] have also been found useful for capillary GC detection.

For wide application of plasma emission chromatographic detection suitable instrumentation must be readily available. Thus, the atmospheric-pressure DC argon plasma (ARL Spectraspan), together with a high-resolution echelle monochromator, has been used for GC detection (GC DCP)[22] for metals and for elements in GC-derivatizing groups such as boron and silicon. Capillary GC detection limits obtained were: for Cr 4 pg/s and selectivity over carbon $4 \cdot 10^8$, for Sn 60 pg/s and $2.5 \cdot 10^6$, for Pb 100 pg/s and $5 \cdot 10^5$ and for B 3 pg/s and $3 \cdot 10^5$ (ref. 23). For individual analyses, GC–DCP and GC–MIP systems have contrasting advantages. The latter is well suited for capillary GC, and its excellent detection limits allow trace determinations of very small samples. However, it has a limited capacity for larger samples, and packed-column applications require solvent venting. The DCP system is somewhat less convenient but accomodates a wider range of sample sizes. For many metals and metalloid elements, the sensitivities of the DCP are close to those of the MIP, and selectivities over carbon are very high.

Despite its wide use as a spectroanalytical emission source, the ICP has seen little use as a GC detector. Windsor and Denton[24] focused their attention upon the elements Br, Cl, F, I, H, Si and C and the metals Sn, Pb and Fe. Detection limits for the latter

were around the ng level, as were those for C and H, but those for F, Cl and Br were at or above the μg level.

Multi-element detection and empirical formula determination

Among the most attractive attribution of element-specific detection is the potential to determine element ratios and, thence, empirical formulae of resolved components at low sample levels. Results and conclusions of various investigators have differed. While some have questioned such determinations because of apparent element response dependency upon molecular structures, and poor detection limits and linearity[25], others have found precision and accuracy to within 1–2% for compounds of similar chemical composition. Thus, Perpall *et al.*[26] used a multi-referencing technique from pyrolysis of known polymers to provide a reproducible range of reference compounds. Linear alkanes, alkenes and alkadienes, produced by pyrolysis of high-density polyethylene, gave relative errors between the actual formula and the experimental formula of 6.7% or less, over the range of C_8 to C_{20} regardless of the hydrocarbon reference chosen. *i.e.* the unknown and the reference compounds did not need to be close in molecular weight. By contrast, these authors found that for pyrolysis of polydimethylsiloxane (PDMS) to a homologous series of cyclic dimethyl-siloxanes, only a narrow reference window could be used, corresponding to one or two homologues, if accurate empirical formulae were to be obtained. Thus there was a need to determine whether the elemental responses for these siloxanes were generally dependent on molecular size and weight of the compound. To accomplish this goal, pyrolysis of an amine-substituted siloxane was carried out, as described below, and empirical formulae of siloxane pyrolyzates of different sizes were calculated. This investigation and other recent studies in our laboraroty, involving operational considerations for different elemental measurements, serve to illustrate the usefulness of this developing technique.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard (Avondale, PA, U.S.A.) 5830A gas chromatograph was used for the pyrolysis experiments with a Hewlett-Packard HP 18835 capillary inlet for split injection. The other injection port supplied helium make-up gas to the interface to induce and sustain the plasma. The capillary column used was 22 m × 0.31 mm I.D., 0.52-μm film thickness, cross-linked 5% phenylmethyl silicone gum (Hewlett-Packard). The atmospheric-pressure multi-channel GC–MIP spectrometer system was as previously desxribed, incorporating a Beenakker type cavity[27], with a modified column–cavity interface to facilitate selctive gas purging[28]. An alumina discharge tube, secured inside a larger quartz tube, was employed for quantitative detection of silicon in the organosilicon compounds. The atomic emission lines selected for this study were: carbon, 247.86 nm, 2nd order; hydrogen, 656.28 nm, 1st order and silicon, 288.16 nm, 2nd order. The pyrolysis was carried out in a Chemical Data Systems (Oxford, PA, U.S.A.) Model 120 Pyroprobe coil-type pyrolyzer with a quartz tube insert. The pyrolysis interface temperature was set to 245–250°C to minimize mass discrimination or thermal decomposition therein. Element-specific responses were displayed on two dual-channel D-4000 Omniscribe chart recorders (Houston Instru-

ments, Austin, TX, U.S.A.), and peak areas were measured by a Model 18850A terminal (Hewlett-Packard).

For inorganic GC, a single-channel GC–MIP system, incorporating a Hewlett-Packard 5840A gas chromatograph and a direct capillary column interface to a Beenakker cavity, was used[30]. A high-resolution grating monochromator[31] or a low-resolution scanning monochromator, having *ca.* 0.1 nm resolution[32] were used, as described previously.

Materials

The amine-substituted PDMS, X2-8124, was obtained from Dow Corning (Midland, MI, U.S.A.). The amine mol percentage was given as 8% by the manufacturer, and the number of silicon-based monomer units in the polymer unit averaged 100.

The chelates, aluminum trifluoroacetylacetonate [Al(TFA)$_3$] and aluminum trifluoroacetylpivalonylmethanate [Al(TPM)$_3$] were prepared by reaction of aluminum nitrate with the respective ligands trifluoroacetylacetone (HTFA) and trifluoroacetylpivalonylmethane (HTPM) (Columbia Organic Chemicals, Columbia, SC, U.S.A.), followed by vacuum sublimation of the products. Cyclopentadienyl rhodium dicarbonyl was obtained from M. D. Rausch of the University of Massachusetts (Amherst, MA, U.S.A.). The samples of derivatized ferrocene boranoates were obtained from C. J. W. Brooks of the University of Glasgow (Glasgow, U.K.).

RESULTS AND DISCUSSION

Empirical formula determination

Simultaneous silicon, hydrogen and carbon element-specific MIP pyrograms were obtained upon pyrolysis of a 500-μg sample of the amine-substituted silicone. Fig. 1 shows pyrograms obtained by heating the sample to 650°C at the maximum rate available for the coil probe (*ca.* 1000°C/s), and holding for 10 s. The column temperature was programmed at 6°C/min from 60 to 300°C. Peaks 1 and 2 are hydrocarbons, peaks 3–8 are the cyclic dimethylsiloxanes, D3–D8, and peaks 9–11 are cyclic siloxanes, incorporating an amine substituent. In earlier work[26] the following expression for the calculation of the element (E)-to-carbon (C) ratio had been used

$$\frac{E}{C} = \frac{E \text{ atoms in reference}}{C \text{ atoms in reference}} \cdot \frac{E \text{ (response of unknown)}}{E \text{ (response of reference)}} \cdot \frac{C \text{ (response of reference)}}{C \text{ (response of unknown)}}$$

This assumed that the sensitivity response factors for each element were equal to unity for all reference compounds. This appeared to be valid for the polyethylene pyrolyzates but not for the silicone pyrolyzates in that study, as was discussed earlier. In the present study, the above equation was modified in two ways. Responses were measured by peak areas rather than peak heights, and each response ratio was modified by including as an exponent the appropriate sensitivity constant for the reference compound, D3, used in the calculation. The sensitivity constants employed were 0.7113 for carbon, 0.7626 for silicon and 0.6982 for hydrogen, obtained from calibration curves measured independently for each element for D3[28]. Table I presents
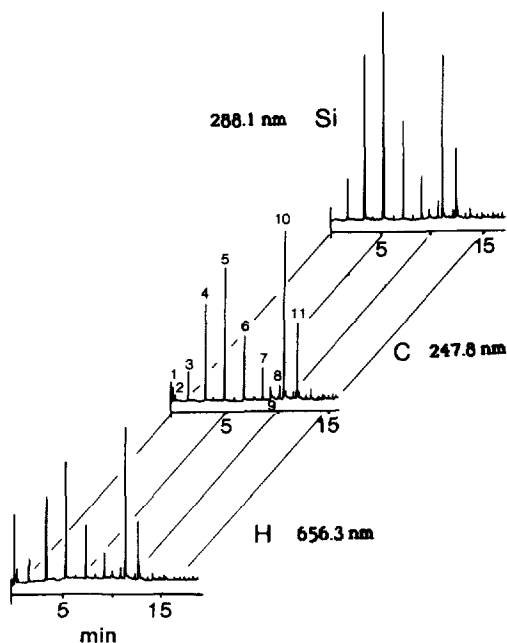
Fig. 1. Simultaneous silicon-, carbon-, and hydrogen-specific detection of pyrolyzates from 0.5 mg of X2-8124 amine-substituted PDMS. Pyrolysis temperature 650°C, held for 10 s. GC column and conditions as in the text, programmed from 60 to 300°C at 6°C/min. Injection temperature, 200°C; pyrolysis interface temperature 300°C. MIP operating conditions: 48 W, helium flow-rate 80 ml/min.

the empirical formulae calculated by this method. It is apparent that the carbon and hydrogen values, referred to silicon, decrease with increasing molecular weights resulting from an increased number of repetition units.

It has been suggested previously that some high-molecular-weight compounds may be incompletely fragmented in the MIP[25]. Our earlier study[26] indicated such a phenomenon for the silicone pyrolysis, and the present results substantiate this

TABLE I

EMPIRICAL FORMULA DETERMINATION OF DIMETHYLCYCLOSILOXANES, PRODUCED BY PYROLYSIS OF X2-8124 AMINE-SUBSTITUTED POLYDIMETHYLSILOXANE

Compound	Empirical formula[a] $Si_1C_{2p}H_{6q}O_1$	
	p	q
$D_3{}^b$	1.00	1.00
D_4	0.97	0.96
D_5	0.94	0.94
D_6	0.92	0.91
D_7	0.91	0.90
D_8	0.90	0.89

[a] Reference peak.
[b] Theoretical empirical formula is $Si_1C_2H_6O$.

conclusion. It would be of interest to assess the ability of a post-column pre-plasma pyrolysis unit, as designed by Chiba and Haraguchi[29], to overcome this problem.

GC–MIP detection in inorganic reaction chemistry

A recent study of ligand interchange between aluminum, gallium and indium complexes has emphasized the value of element specific GC detection for following such reactions[30]. As a further example of element-specific GC detection, Figs. 2 and 3 show carbon and aluminum specific chromatograms of a solution of two aluminum chelates, Al(TFA)$_3$ and Al(TPM)$_3$, before and after ligand redistribution in dichloromethane solution at 25°C for 24 h. It is of interest to note that the peak shapes observed for the aluminum chelates at the aluminum line at 396.2 nm, exhibit less tailing than those measured at the carbon line. This suggests that peak broadening in the carbon channel reflects memory effects in the plasma rather than chromatographic interactions on the column.

GC–MIP has proved valuable in the study of volatile organometallic compounds. Now reported are initial studies on rhodium-specific detection, which has not previously been described. The emphasis here is on the choice of the emission line, which may be dictated by either sensitivity or selectivity considerations. Rhodium lines, suited for GC monitoring, were established first by bleeding a low level of volatile cyclopentadienyl rhodium dicarbonyl [CpRh(CO)$_2$] into the MIP at a constant rate. The two preferred spectral lines for analysis proved to be at 343.5 nm [Rh(I)] and 249.1 nm [Rh(II)]. The GC–MIP parameters were optimized by repetitive injections into the
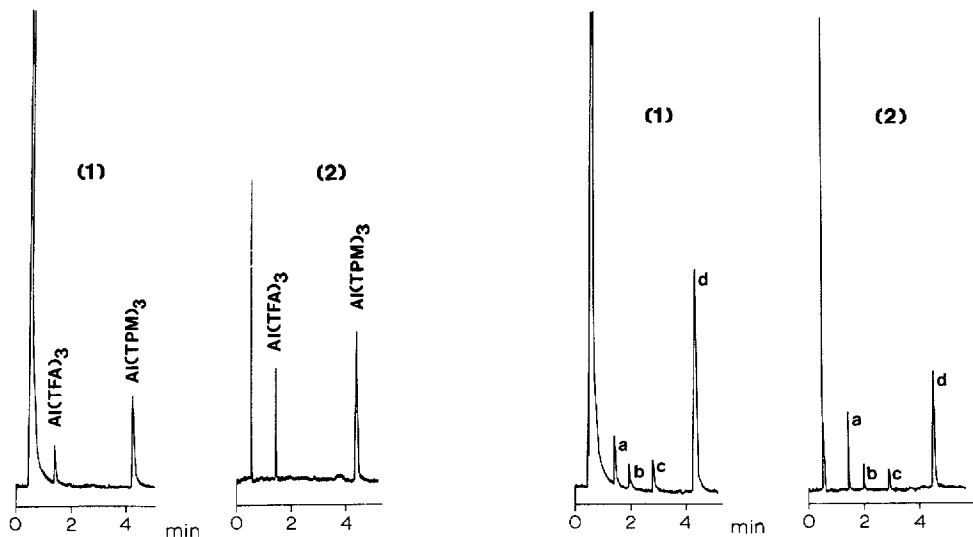

Fig. 2. Dual sequential carbon [(1), 247.8 nm] and aluminum [(2), 396.2 nm] detection of aluminum trifluoroacetylacetonate and trifluoroacetylpivalonylmethanate. Column, 10 m × 0.25 mm I.D. SE-30 (fused-silica open-tubular); column temperature, 130°C.

Fig. 3. Dual sequential carbon [(1), 247.8 nm] and aluminum [(2), 396.2 nm] detection of redistribution products of aluminum chelates after 24 h in dichloromethane at 25°C. Column and conditions as for Fig. 2. Key to peaks: a = Al(TFA)$_3$; b = Al(TFA)$_2$(TPM); c = Al(TFA)(TPM)$_2$; d = Al(TPM)$_3$.

capillary column. The linear response range at 343.5 nm was more than three orders of magnitude, and the detection limit at a signal-to-noise ratio of 3 was 211 pg of the metal.

In Fig. 4 is shown a comparison of chromatograms for the two most useful wavelengths for rhodium emission. The test solution contained 0.34 g of *n*-nonane and 0.067 g of the rhodium compound dissolved in 1 ml of hexane. Selectivity over carbon at 343.5 nm was *ca.* 1100, based on an *n*-nonane response in the linear range. However, the selectivity at 249.1 nm was in the region of 4000, whereas the sensitivity was approximately one order of magnitude less that for the longer wavelength. The choice of emission wavelength here depends on the relative importance of detection limits and the nature of the sample matrix.

Element-specific functionality derivatization

The idea of chromatographic analysis for chemical functionalities through their derivatization with a reagent, containing a particular analyte element or elements, has been introduced earlier[11]. We have undertaken a preliminary exploration of such an approach for cyclic ferroceneboronate derivatives. Brooks and Cole[33] have shown these to be produced quantitatively from reactions of ferroceneboronic acid with 1,2- and 1,3-diols, these compounds giving good GC peak characteristics. A GC–MIP investigation of the same pinacol and dicyclohexyl-1,1′-diol ferrocene boronates as were studied with GC–MS by Brooks and Cole[33] showed a typical pair of chromatograms as in Fig. 5. A mixture of the derivatives at a molar ratio of 0.730 gave responses for iron at 259.94 nm and boron at 249.68 nm. Hydrogen was doped into the
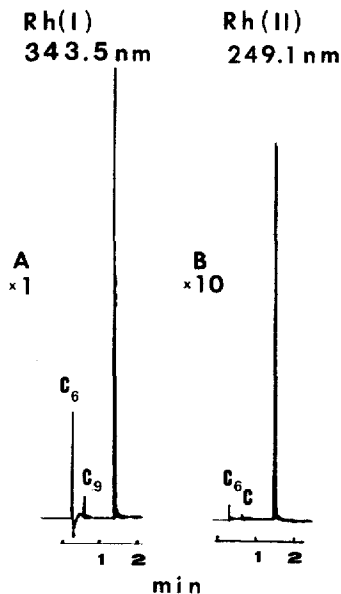

Fig. 4. GC–MIP detection of rhodium in rhodium cyclopentadienyl–dicarbonyl at 343.5 and 249.1 nm. Column, 11 m × 0.20 mm I.D. SE-30 (fused-silica open-tubular); column temperature, 110°C. MIP operating conditions: 70 W, helium flow-rate 500 ml/min. The sensitivity setting for B is ten times that of A.
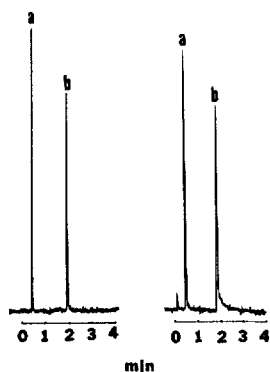
Fig. 5. Dual sequential iron (left, 259.94 nm) and boron (right, 249.68 nm) detection of pinacol ferroceneboronate (a) and dicyclohexyl-1,1'-diol ferroceneboronate. Column, 12 m × 0.32 mm I.D. DB-5 (fused-silica open-tubular); column temperature, 210°C for 30 s, then programmed at 30°C/min to 260°C.

plasma at *ca.* 1 ml/min to reduce peak tailing for the boron response, attributable to deposition of boron in the plasma-discharge tube[34]. Table II shows peak area ratios for iron and boron responses at different sample levels, indicating a consistent elemental response. In this case, boron and iron appear to show very similar absolute sensitivities, although the iron line may be preferred for quantitative studies because of the better GC peak shapes.

The potential utility of this type of elemental derivatization is considerable, particularly when the elements introduced into the analyte molecules, here the diols, are unlikely to be encountered in the remainder of the chromatogram.

TABLE II

RESPONSE RATIOS (PEAK AREAS) FOR PINACOL FERROCENEBORONATE AND DICYCLO-HEXYL-1,1'-DIOL FERROCENEBORONATE, MEASURED AT IRON AND BORON LINES

Amount injected (pmol)		Molar ratio (P:D)	Ratio of peak areas (P:D)	
Pinacol ferrocene boronate (P)	Dicyclohexyl-1,1'- ferroceneboronate (D)		Fe Line	B Line
92.0	126	0.730	0.716	0.740
30.7	42.0	0.730	0.782	
16.7	22.9	0.730	0.878	0.772
5.58	7.64	0.730	0.800	

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