lecular weight (171) as C₃ quinoline, but no tertiary amine substituted naphthalenes exist which correspond to C_0 , C_1 , and C₂ substituted quinolines, which have molecular weights of 129, 143, and 157, respectively. However, from the C_3 substituted azaarene and beyond, there is a possibility of tertiary aromatic amines being present as well as azaarenes. Thus, these assignments cannot be made with certainty.

Both the ESB and the acetone subfraction contained primary aromatic amines (PAAs). There were more kinds of PAAs detected in the acetone subfraction than in the original ESB as was intended (1, 9) by the separation procedure used. Secondary aromatic amines were only detected in the ESB fraction. As in the case of the tertiary-type amines, it is not possible to assign these conclusively as either heterocyclic or amine-substituted aromatics.

The NH₃/ND₃ CI technique has been shown to be useful in the mass spectral analysis of primary, secondary, and tertiary amine substituted aromatics as well as nitrogen heterocycles in complex samples. Heterocyclic nitrogen compounds cannot be unambiguously distinguished from amines using NH₃/ND₃ CI, unless additional information is obtained from either the sample history or other spectroscopic techniques.

An additional feature of the NH_3/ND_3 CI technique is that only compounds with proton affinities greater than NH_4^+ (207) kcal/mol) are ionized; thus this technique can be used to characterize nitrogen-containing compounds in the presence of other types of compounds in a mixture (including-OH and -SH substituted) without interference (10).

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Determination of Organosulfur Compounds in Hydrocarbon Matrices by Collision Activated Dissociation Mass Spectrometry

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Collision activated dissociation mass spectra of $(M + 1)^+$ lons from 33 organosulfur compounds are presented. Ions resulting from loss of the radical HS- are prominent in the spectra of thiophenois, dithienyis, trithienyis, and dibenzothiophene derivatives but not in the spectra of aliphatic sulfides or highly alkylated thiophenes. Use of 33 amu neutral loss scans on a triple quadrupole mass spectrometer for the analysis of organosulfur compounds in crude petroleum distillates is described. Total time per sample for this analysis is under 20 min. Qualitative differences in the spectra of several crude oil samples are readily apparent. Preliminary results from collision activated dissociation of $(M + NO)^+$ lons in the nitric oxide chemical ionization mass spectra of aliphatic sulfones are described.

Potential shortages of high-quality crude petroleum that can be easily processed as fuel have prompted investigations into alternate energy sources such as heavy petroleum distillates, coal liquids, shale oil, and oil from tar sands. Detailed knowledge of the chemical components present in these materials is necessary in order to ensure that the most effective. efficient and environmentally safe methods are chosen for production, storage, and processing of these valuable resources. Monitoring organosulfur compounds during fuel production

is important since many of these compounds poison the catalysts used in the processing steps, several of the sulfur heterocycles are suspected mutagens and/or carcinogens (1), and toxic gases such as H_2S and SO_2 are liberated during utilization of fuels rich in sulfur-containing components.

Analytical methods for characterizing sulfur compounds in coal liquids, shale oil, and crude petroleum currently involve extensive fractionation of the sample by a combination of distillation, extraction, and chromatographic steps followed by analysis with either a gas chromatograph/mass spectrometer system (2-5) or a double focusing mass spectrometer operated under low voltage EI $(12 \pm 0.2 \text{ eV})$ conditions at a resolution in excess of $50\,000$ (6, 7). Gas chromatography/mass spectrometry is ideally suited for the identification of specific structural isomers in highly fractionated samples but is too time-consuming for routine characterization of complex petroleum matrices. In contrast, direct analysis of petroleum feedstock or coal liquefaction products by low-voltage electron-impact, high-resolution mass spectrometry can be accomplished relatively quickly and affords a wealth of information about the elemental composition, molecular weight, and carbon number of the mixture components. This method affords excellent results for hydrocarbon matrices rich in compounds containing the elements C, H, N, and O but is much less satisfactory for characterizing mixtures rich in sulfur compounds. In this situation extremely high resolving power, Here we outline preliminary results of a research effort to develop a rapid qualitative survey analysis of sulfur compounds which is transparent to hydrocarbon matrices and which affords the relative abundance and molecular weight of the organosulfur compounds plus information about the structural environment of the sulfur atom in the molecules under analysis. The combination of chemical ionization and collision activated dissociation on a Finnigan triple quadrupole mass spectrometer is utilized in this work which, in turn, is part of a much larger effort to develop a master scheme for the analysis of organics in mixtures by functional group.

Recently, a number of reviews have appeared that detail the general utility of collision activated dissociation on a tandem mass spectrometer for the direct analysis of mixtures (8-11). A communication describing efforts to detect sulfur heterocycles in the presence of aromatic hydrocarbons of the same nominal mass by metastable analysis has also been published (12).

EXPERIMENTAL SECTION

The instruments employed in the present study were a triple stage quadrupole mass spectrometer/data system manufactured by Finnigan Corp., Sunnyvale, CA, and a Finnigan triple quadrupole instrument constructed in this laboratory. The latter instrument has been described previously (13). Instrumental Parameters. The mass spectrometers were

Instrumental Parameters. The mass spectrometers were operated under chemical ionization conditions in the positive ion mode with methane and nitric oxide as the reagent gases. Bombardment of methane at 0.5 torr generates the reactant ions CH_5^+ and $C_2H_5^+$. Production of NO⁺ from nitric oxide at 0.5 torr is accomplished with a Townsend discharge that has been described previously (14, 15). All samples were coated on the tips of glass rods and inserted into the ion source by way of a heated solids probe. Argon of 99.97% purity from Matheson Corp. was employed as the collision gas at a pressure of 1–4 mtorr in all collision activated dissociation experiments. Ion energies were in the range of 10–20 eV.

Daughter Ion Scans. Collision activated dissociation mass spectra of the $(M + 1)^+$ and $(M + 30)^+$ ions in the methane and nitric oxide chemical ionization spectra of organosulfur compounds were obtained by setting quadrupole 1 to transmit the ion of interest, filling the collision cell containing quadrupole 2 with argon, operating quadrupole 2 in the radio frequency (rf) only mode (13), and scanning quadrupole 3 to collect all daughter ions produced in the collision activated dissociation process.

Neutral Loss Scans on Crude Oil Samples. Qualitative analysis of crude petroleum distillates for organosulfur compounds which lose the neutral moiety HS· under collision activated dissociation conditions was accomplished by scanning quadrupole 1 and quadrupole 3 repetitively every 2 s over the desired mass range at a fixed mass separation of 33 amu while 1 mg of oil was volatilized into the ion source from a heated solids probe. Spectra recorded in this mode contain only daughter ions produced by loss of HS· in quadrupole 2. Results presented in Figure 1 were obtained by summing all spectra acquired during the lifetime of the sample in the ion source.

Chemicals. All samples were either purchased from the Aldrich Chemical Co. or obtained as gifts from the Shell Development Corp., Houston, TX.

Preparation of Sulfones. Oxidation of sulfides to sulfones was accomplished by treating the sample in methylene chloride with an excess of *m*-chloroperbenzoic acid for 5 min at room temperature. Excess acid was removed by extraction with 10% NaHCO₃. Following evaporation of the methylene chloride under a stream of nitrogen, the sample was placed on the tip of a glass rod and inserted into the ion source via a heated solids probe.

RESULTS AND DISCUSSION

The combination of chemical ionization and collision activated dissociation on a tandem mass spectrometer such as the Finnigan triple quadrupole instrument has tremendous



Figure 1. Collision activated dissociation mass spectra obtained in the 33 amu neutral loss mode on $(M + 1)^+$ ions from organosulfur compounds in (A) South Swan Hills, (B) Prudhoe Bay, and (C) Gack Saran crude oils. Signals at m/z 134, 152, and 216 are due in part to residual lon current from a mixture of compounds 3, 7, and 6 used to set up the instrument for 33 amu neutral loss scans.

potential for rapid qualitative analysis of organics in complex matrices. Two modes of operation, the neutral loss scan and the parent ion scan are particularly well suited for this type of analysis. Chemical ionization is employed to convert matrix components to ions characteristic of sample molecular weight and to minimize subsequent fragmentation of the sample ions in the ion source. The neutral loss scan mode involves setting quadrupole 1 and quadrupole 3 to scan repetitively at a fixed mass separation over the desired mass range. Under these conditions the only ions which are transmitted through quadrupole 3 are those that are mass selected by quadrupole 1 and suffer loss of a neutral of specific mass in the collision activated dissociation process in quadrupole 2. In cases where the neutral loss is uniquely characteristic of a particular functional group, this scan mode can be employed to selectively analyze all members of a specific class of compounds Table I. Collision Activated Dissociation Mass Spectra of $(M + 1)^*$ Ions from Organosulfur Compounds Generated under Positive Ion Chemical Ionization Conditions

							% total sample ion current
no ^a	mol wt	(M +	-H	-SH	-CS	-80	
110.		±)	**	511	00		otner, m/z (%)
1	160	26.7		73.3			
2	128	22.7		13.7			65 (9.1), 95 (13.6), 109 (40.9)
3	166	8.6		47.6	28.6		45 (4.7), 77 (1.0), 79 (9.5)
4	166	27.4		50.8	19.3		79 (2.5)
5	248	9.2		41.7	1.7		97 (8.8), 109 (4.2), 121 (2.1), 127 (9.2), 134 (1.7), 153 (4.2), 165 (1.7), 171 (9.2), 184 (2.1), 190 (2.5), 203 (1.7)
6	248	9.1		43.3			97 (8.7), 109 (3.5), 121 (1.3), 127 (9.5), 134 (1.3), 153 (4.3), 165 (1.6), 171 (10.0), 184 (2.6), 190 (2.6), 203 (2.2)
7	184	42.1	45.6	7.0			115 (1.8), 139 (3.5)
8	190	22.2	3.8	74.0			
9	260	24.0	9.1	30.7	1.5		127 (1.2), 152 (18.2), 183 (3.0), 184 (3.9), 202 (1.2), 215 (3.0) 245 (1.5), 246 (2.7)
10	286	29.0		47.5			165 (2.5), 209 (4.0), 210 (2.5), 239 (2.0), 253 (12.5)
11	240	17.0	70.0	4.8	4.8		164 (3.4)
12	290	17.5	50.0	32.5			
13	290	47.7	42.8	9.5			
14	290	29.5	56.8	13.7			
15	190	9.7	7.3		80.6		103 (1.6), 115 (0.8)
16	236	46.5		32.6			103 (2.3), 128 (2.4), 159 (2.3), 191 (2.3), 191 (2.3), 222 (11.6)
17	162	9.0	7.5				91 (2.5), 115 (2.5), 119 (2.0), 135 (7.5), 147 (19.0), 148 (50.0)
18	352	1.9					43 (3.7), 57 (26.9), 71 (18.5), 85 (11.2), 185 (37.5), 213 (0.3)
19	176	14.0					128 (2.8), 129 (2.2), 142 (2.8), 147 (11.2), 161 (11.2), 162 (55.8)
20	168	1.2					41 (6.3), 43 (42.0), 57 (18.9), 85 (18.9). 99 (7.6)
21	168	4.8					29 (1.9), 41 (9.6), 57 (48.3), 85 (8.7), 93 (1.9), 99 (1.9), 113 (20.5) 127 (2.4)
22	224	1.2					41 (3.1), 43 (26.8), 57 (39.1), 71 (10.9), 85 (13.7), 99 (5.2)
23	224	6.5					43(14.0), 57(31.8), 71(24.8), 85(3.8), 113(15.9), 127(3.2)
24	102	5.0					41 (2.0), 55 (5.0), 57 (4.0), 61 (84.0)
25	146	3.5					29 (3.5), 41 (14.1) 57 (70.4), 63 (1.5), 91 (7.0)
26 ^b	246						109 (10.0), 135 (10.0), 137 (80.0)
27 6	274						123 (16.0), 151 (84.0)
28	216	16.9				50.6	152 (18.2), 161 (1.3), 168 (6.5), 171 (2.6), 184 (1.3), 200 (2.6)
29	292	3.8				3.8	215 (3.8), 244 (84.8), 260 (3.8)
30	354	35.7				22.9°	$\begin{array}{c} 226 \ (17.1), \ 234 \ (1.4), \ 235 \ (2.2), \ 242 \ (8.6), \ 258 \ (2.2), \ 262 \ (1.4), \\ 273 \ (2.9), \ 274 \ (2.8), \ 307 \ (1.4), \ 339 \ (1.4) \end{array}$
31	218	16.7					77 (33.3), 91 (12.5), 93 (12.5), 141 (25.0)
32	246						77 (4.8), 91 (61.6), 141 (3.1), 181 (22.6), 219 (4.8)
33	402	9.1					43 (9.1), 57 (22.7), 71 (18.2), 85 (9.1), 235 (31.8)
^a Nun	ibers r	efer to a	structur	es in Fi	gure 2.	^b Collisi	ion activated dissociation mass spectrum of the M^+ ion. $c -2SO_2$

molecules.

in a complex matrix. Loss of 44 amu (CO₂) from $(M - 1)^{-1}$ ions is highly characteristic of carboxylic acids (16). Accordingly, 44 amu neutral loss scans on the triple quadrupole can be employed for the direct analysis of these compounds in urine (17).

In the parent ion scan mode, quadrupole 3 is set to pass only ions of a particular m/z value while quadrupole 1 is scanned over the desired mass range. To be detected an ion of a particular mass in the ion source must be transmitted by quadrupole 1, suffer collision activated dissociation in the collision cell, quadrupole 2, to a specific fragment which is then transmitted through quadrupole 3. $(M + 1)^+$ ions from all phthalates, except dimethyl phthalate, suffer collision activated dissociation with loss of the alkyl groups to produce a fragment ion at m/z 149. Accordingly, only the $(M + 1)^+$ ions of phthalates are detected when a mixture is analyzed using parent ion scans with quadrupole 3 set at m/z 149 (18).

Development of a satisfactory analysis for sulfur compounds in the presence of aromatic hydrocarbons requires that a combination of ionization conditions, ion-molecule reactions and/or derivatization steps be employed to direct fragmentation of the sample along a pathway which involves either elimination of a neutral containing sulfur or formation of a charged species characteristic of all or specific types of sulfur-containing compounds. Initial efforts toward this goal have examined the possibility of using methane as the reagent gas under positive ion chemical ionization conditions and collision activated dissociation of the resulting $(M + 1)^+$ ions.

Collision Activated Dissociation Mass Spectra of $(M + 1)^+$ Ions. Mass spectral data from collision activated dissociation of $(M + 1)^+$ ions from 33 organosulfur compounds are presented in Table I. Many of the benzothiophene type compounds lose H· under the low energy (10-20 eV) collision activated dissociation conditions employed in the triple quadrupole instrument (eq 1). Ions resulting from the loss

$$\underbrace{\bigcirc}_{\substack{+,s' \\ +, s' \\ +, t'}} \underbrace{\bigcirc}_{M^{\dagger}} \underbrace{\odot}_{M^{\dagger}} \underbrace{\bigcirc}_{M^{\dagger}} \underbrace{\odot}_{M^{\dagger}} \underbrace{\odot}_{M^{\bullet$$

of the radical HS- are prominent in spectra of the thiophenols, 1 and 2, the dithienyls, 3 and 4, the trithienyls, 5 and 6, the dibenzothiophene derivatives, 7-14, thienobenzothiophene, 15, and diphenylthiophene, 16 (eq 2). In contrast spectra of

$$\underbrace{\bigcirc}_{H} \underset{H}{\overset{H}{\longrightarrow}} \rightarrow \underbrace{\bigcirc}_{SH} \underset{SH}{\overset{H}{\longrightarrow}} \rightarrow \underbrace{\bigcirc}_{SH} \underset{H}{\overset{H}{\longrightarrow}} \rightarrow \underbrace{\bigcirc}_{H} \underset{H}{\overset{H}{\longrightarrow}} \overset{I^{+}}{\longrightarrow} \underset{M^{+} : 33^{+}}{\overset{H^{+}}{\longrightarrow}} (2)$$

highly alkylated sulfur heterocycles, 17–23, and the aliphatic sulfides, 24–27, are rich in hydrocarbon fragment ions and



Figure 2. Structures of organosulfur compounds. Numbers refer to compounds in Tables I and III.

devoid of ions resulting from loss of HS. Signals corresponding to the elimination of C=S are observed in the spectra of the polythienyl compounds, 3-5. Observation of a 1/1 doublet corresponding to loss of C³²S and C³⁴S from the $(M + 3)^+$ ion in the collision activated dissociation mass spectrum of 3 confirms the composition of the neutral moiety ejected in this fragmentation process (eq 3).

Neutral Loss Scans on Crude Oil Samples. On the basis of the above data we conclude that 33 amu neutral loss scans can be used to survey at least the thiophenols, polythienyls, and dibenzothiophene type compounds in a hydrocarbon matrix. Initial results of analyses performed on high boiling crude oil distillates are presented in Figure 1. Since loss of 33 amu appears to be unique to sulfur heterocycles, each signal in these spectra should correspond to a thiophenol or dibenzothiophene type compound whose molecular weight is 32 amu higher than that of the ion observed. Note that the signals at m/z 134, 152, and 216 are due in part to residual ion current from a mixture of compounds 3, 7, and 6 used to set up the instrument for a 33 amu neutral loss scan. Signals for these internal standards correspond to levels in the range of 50-400 ng of material. A partial list of possible structural assignments for the ions in the South Swan Hills sample is presented in Table II.

Qualitative differences on both the molecular weight distribution and structural type of sulfur compounds present in the samples are readily apparent from the three spectra. We find these results to be quite encouraging given that the data were obtained in less than 20 min by direct analysis of 1 mg of crude oil distillate. Much work with model compounds, known mixtures of standards, and hydrocarbon mixtures characterized by other methods remains before the real value of the above approach can be determined. Short comings of

Table II. Possible Structural Assignments for Ions Observed in 33 amu Neutral Loss Scans on the 375-535 $^{\circ}$ C Distillation Fraction from South Swan Hills Crude Oil

compounds: alkylated	m/z series
phenylthiophenes naphthalenethiols naphthenobenzothiophenes	128, 142, 156, 170
naphthylthiophenes phenylbenzothiophenes phenanthrenethiols anthracenethiols thienoacenaphthalenes naphthenodibenzothiophenes	178, 192, 206, 220, 234, 248
naphthobenzothiophenes pyrenethiols thienophenanthrenes thienoanthracenes trithienyls	202, 216, 230, 244, 258, 272
thienopyrenes benzothienoacenaphthylenes thienofluoranthenes triphenylenothiophenes	226, 240, 254, 268, 282, 296
chrysenethiols benzothienoacenaphthalenes naphthenothienophenthrenes	228, 242, 256, 270, 284, 298
thienofluorenes naphthenothienoacenaphthalenes	$\begin{array}{c} 190,204,218,232,\\ 246,260 \end{array}$
dinaphthothiophenes benzopyrenethiols naphthenothienopyrenes	252, 266, 280, 294, 308
benzotriphenylenothiophenes benzoperylenethiols thienobenzopyrenes benzothienofluoranthenes	276, 290, 304, 318
azophenanthrenethiols pyridylbenzothiophenes thienoazaacenaphthalenes	179, 193, 297, 221, 235
thienocarbazoles	191, 205, 219, 233
thienophenthropyrrole azabenzothienoacenaphthalene	215, 229, 243, 257

the methodology are already apparent in that $(M + 1)^+$ ions of highly alkylated sulfur heterocycles and aliphatic sulfides fail to lose HS- under collision activated dissociation conditions.

Collision Activated Dissociation Mass Spectra of Sulfone $(M + 1)^+$ Ions. To overcome the former problem, we have examined the possibility of derivatizing the sulfur compounds to enhance the probability of both ionization and fragmentation occurring in the vicinity of the sulfur functionality. Oxidation of sulfides, except thiophenes, to sulfones with m-chloroperbenzoic acid occurs in good yield. That this may well be a promising approach is shown by the results obtained on the sulfone derivative of dibenzothiophene, 28. More than 50% of the sample ion current in the collision activated dissociation mass spectrum of the $(M + 1)^+$ ion from **28** is carried by a fragment formed by loss of 64 amu (SO_2) . In contrast the fragment formed by loss of 33 amu (HS-) from the $(M + 1)^+$ ion of the parent sulfide, 7, carries only 7% of the total sample ion current. The disulfide compound, 30, loses two molecules of SO_2 under the above experimental conditions. Predictably, collision activated dissociation mass spectra of $(M + 1)^+$ ions from aliphatic sulfones are rich in hydrocarbon fragments. Loss of SO_2 is not observed for these compounds.

Collision Activated Dissociation Mass Spectra of Sulfone $(M + NO)^+$ Ions. Another potentially useful approach for the analysis of organosulfur compounds in hy-

	${f mol} {f wt}$	% total sample ion current						
no. <i>ª</i>		(M + NO) ⁺	M+·	NO ⁺	other m/z			
28	216	5.0	22.5		160 (12.5), 168 (5.0), 171 (5.0), 172 (5.0), 187 (15.0), 188 (10.0)			
32	246	2.0	2.0		91 (58.0), 104 (12.0), 182 (24.0), 212 (2.0)			
31	218	1.0	1.0	45.0	77 (1.5), 97 (1.0), 125 (48.5), 131 (2.0)			
33	402			8.3	43 (3.3), 55 (3.3), 57 (6.7), 69 (13.4), 71 (8.3), 83 (10.0), 85 (6.7), 97 (16.7), 111 (16.7), 125 (3.3), 167 (3.3)			
34	170	6.7		86.6	78 (1.7), 94 (3.3), 108 (1.7)			
35	184	10.0		76.0	78(4.0), 108(2.0), 125(6.0), 142(2.0)			

Table III. Collision Activated Dissociation Mass Spectra of $(M + NO)^+$ Ions from Organosulfur Compounds Generated under Nitric Oxide Chemical Ionization Conditions

drocarbon matrices involves the use of the nitrosonium ion (NO⁺) as a chemical ionization reactant. Previously NO⁺ has found utility for the analysis of alkanes (19), olefins (20), and alcohols (21), as well as for enhancing the abundance of the molecular ion in spectra of biological compounds (22, 23). In the gas phase the nitrosonium ion functions as an electron acceptor, hydride and hydroxide abstractor, and electrophile toward organic molecules (24).

One electron transfer is observed when the ionization potential of the sample is less than the recombination energy of the NO⁺ ion. Einolf and Munson have estimated the latter quantity at 8.3 eV (22) (eq 4). Experimentally we observe that most aromatic hydrocarbons undergo the one electron transfer reaction with NO⁺ (eq 5). Formation of $(M + NO)^+$ ions is also observed.

$$NO^+ + e^- \rightarrow NO \qquad \Delta H = -8.3 \text{ eV}$$
 (4)

$$C_{10}H_8 + NO^+ \rightarrow C_{10}H_8^+ + NO$$
 (5)

In the case of sulfones, ions resulting from electrophilic addition of NO⁺ are formed in high abundance. Mass spectral data from collision activated dissociation of sulfone $(M + NO)^+$ ions are shown in Table III. Dissociation occurs at the sample-NO bond with the charge preferentially or exclusively residing on the neutral having the lowest ionization potential. In the case of the dibenzothiophene sulfone, 28, or dibenzyl sulfone, 32, collision activated dissociation produces the corresponding M⁺ as well as several smaller fragment ions but no nitrosium ions (eq 6). In contrast, dissociation of (M +NO)⁺ ions with charge retention on the NO moiety is a major pathway for fragmentation of aliphatic sulfones (eq 7). These results suggest that parent ion scans with quadrupole 3 set to monitor m/z 30 (NO⁺) will facilitate analysis of sulfones from aliphatic sulfides in the presence of other sulfur heterocycles and polycyclic aromatic hydrocarbons.

$$(6)$$

$$EtSO_2(NO)Ph^+ \xrightarrow{Ar} EtSO_2Ph + NO^+$$
 (7)

Future work will evaluate the utility of combining the m-chloroperbenzoic acid oxidation step with analysis of the resulting sulfones using a mixture of chemical ionization reagent gases composed of methane and nitric oxide plus both neutral loss and parent ion scans on the triple quadrupole instrument. Nitric oxide will be added to the methane in sufficient quantities to generate equal amounts of CH_5^+ and NO⁺. Collision activated dissociation mass spectra acquired in the 64 amu neutral loss mode and parent ion scans of NO⁺ will be employed to monitor benzothiophene type compounds and aliphatic sulfides, respectively. Since these modes of operation can be alternated every 1 or 2 s under computer control on the Finnigan triple quadrupole, rapid determination of sulfur compounds in complex hydrocarbon matrices should be achieved. Total analysis time per sample should not exceed 30 min.

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