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Determination of sulphur and nitrogen gases by gas chromatography on polystyrene porous polymer columns

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ABSTRACT

The performance of various Chromosorb Century Series porous polymer bead stationary phases for the simultaneous determination of sulphur and nitrogen gaseous compounds was investigated. The separation at different temperatures of H_2S, COS, SO_2, N_2O, NO, NO_2, CO_2, H_2O, NH_3, CH_4, C_2H_2, C_2H_4, C_2H_6 and C_3H_8 was carried out over wide concentrations ranges using thermal conductivity and helium ionization detectors. Retention times and retention index values on polystyrene and styrene–divinylbenzene polymers (Chromosorb 101, 102, 103 and 106) are given. The effect of contamination of the sample and of the system, contamination of the carrier gas, adsorption and reaction of the sample and area losses due to the integration method on the accuracy of determinations at low concentrations was investigated.

INTRODUCTION

The gas chromatographic (GC) determination of sulphur and nitrogen gases (H_2S, COS, SO_2, NH_3, N_2O, NO, NO_2) has previously been carried out by many workers with different detectors and stationary phases [1–33]. From the early commercial availability of porous polymer beads (PPBs), these polymeric phases were considered a good choice for the determination of reactive gases, owing to their low polarity [34,35] and good stability [36–47]. Previous studies on the determination of trace amounts of these gases by using a Porapak Q column and a helium detector were published in 1969 [48]. Surprisingly, for some years the application of porous polymers to the simultaneous determination of trace amounts of sulphur and nitrogen gases was neglected, probably owing to the difficulty of operating the helium detector under routine conditions, as it is very sensitive to carrier gas impurities and to microscopic leakages in the pneumatic circuit. On the other hand, the flame photometric detector, which is very sensitive to sulphur compounds, does not permit the determination of nitrogen compounds.

More recently, the introduction of detectors stable and sensitive enough to reach the ppm range under routine conditions (amplified micro thermal conductivity detectors) led to the application in industry of GC methods for the simultaneous determination of sulphur and nitrogen gases in samples of different origin and concentration (process and exhaust gases, controlled atmosphere for metallurgy and electronics, environmental monitoring, etc.).

Industrial and environmental applications often require automatic sampling and computerized data handling, and sometimes yield poorly reproducible results in the analysis of low-concentration samples, which is generally ascribed to adsorption or decomposition phenomena taking place in the sampling system or in the column [2,13,49,50].

Many types of PPBs with different polarities have been used and various advantages were claimed for particular applications. It therefore seemed useful to compare under reproducible conditions the performances of the various PPBs available, and to investigate the effects of different phenomena on the accuracy of analyses at low concentrations.

In the work described here, the Chromosorb Century Series (Johns-Manville, Denver, CO, USA)

porous polymers, the polarity and batch-to-batch reproducibility of which have been investigated previously [51], were tested for the separation of sulphur and nitrogen gases, the performances of polystyrene types mainly being considered.

EXPERIMENTAL

Stainless-steel, glass and PTFE columns (3 m × 2.4 mm I.D.) were filled with Chromosorb Century Series types 101, 102, 103, 104, 105, 106, 107 and 108 (80–100 mesh) and conditioned at 150°C for 4 days or more under a helium flow. The samples contained different amounts of the following compounds, diluted in helium: H_2S, COS, SO_2, N_2O, NO, NO_2, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and H_2O. The alkanes permitted the measurement of the Kováts retention index, while ethylene, CO_2 and acetylene were used in order to evaluate the polarity of the columns, following the procedure suggested previously [52,53].

Samples at different concentrations were prepared by mixing in PTFE or Mylar bags different amounts of pure gases, delivered from glass syringes of various volumes (1–100 ml). The sampling systems, tubings, sample loops, etc., were made of PTFE or nylon and, when metal or glass connections were unavoidable, they were deactivated by silanization. Low-concentration samples were prepared by using the exponential dilution flask technique [54,55], by starting from an initial concentration of 100 or 200 ppm and going down to the ppb[a] level, until memory effects, vacancy chromatography and other non-linear phenomena were observed (see below).

The analyses were carried out at different temperatures ranging from 30 to 100°C. All of the test compounds were examined over the whole temperature range, in steps of 20°C in the range 30–70°C and of 15°C for higher temperatures. Slowly eluting compounds (H_2O, SO_2, NH_3 and COS) on more polar columns were mainly studied in the range 70–100°C, where their elution times are shorter and the resulting peaks more symmetrical.

An amplified-output thermal conductivity detectors installed in a Model 3700 gas chromatograph

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[a] Throughout this article, the American billion (10^9) is meant.

(Varian, Palo Alto, CA, USA) was used for most of the analyses. The conditions were as follows: detector block temperature, 120°C; detector filament temperature, 300°C; detector filament current, 340 mA; and sensitivity range, 0.05. At the highest sensitivity range it permitted the detection of 0.1–0.2 ppm of O_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_2H_2 [56], NO, N_2O and H_2S. A lower sensitivity to SO_2, H_2O, NH_3 and NO_2 was observed, mainly owing to unfavourable peak shapes or longer retention times. In order to investigate the behaviour of the column at the lowest sample concentrations, with respect of memory effects and vacancy chromatography phenomena, a helium detector (Varian), originally designed for installation on the Varian Model 1532 trace gas analyser and modified to fit the Model 3700, was also used in some experiments and operated at a voltage of −400 V ± 10 mV [48,57,58].

Pure-grade helium, further purified through a molecular sieves trap immersed in liquid nitrogen for the analyses of low-concentration samples with helium detection (HeD) and highly amplified thermal conductivity detection (TCD) and for calibration with the exponential dilution flask, was used as the carrier gas, at a flow-rate of 22 cm^3/min, kept constant by proper adjustment after equilibration of the column at each temperature. This carrier gas flow-rate was selected because previous experiments showed that it corresponds to the minimum of the Van Deemter–Jones plot, i.e., the highest column efficiency. The maximum HeD sensitivity was not achieved at this flow-rate, because the sub-ppb range required about 60 cm^3/min of pure helium, but a sensitivity in the 2–10 ppb concentration range was sufficient for the planned experiments.

Integration of the peaks was carried out by using different integration devices and data systems, or by manual triangulation and height/width measurements, in order to investigate the effect of integration methods on the accuracy at low concentration.

RESULTS AND DISCUSSION

The adsorption or decomposition phenomena often indicated as the cause of the anomalous response of reactive gases on porous polymer columns were found to be a real problem for polar compounds on some polymers. The producer re-
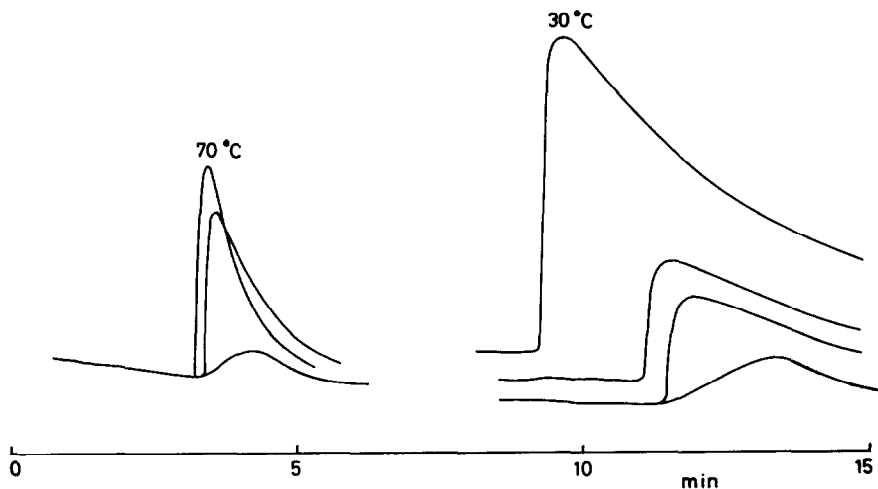
Fig. 1. Asymmetry of NH₃ peak at various concentrations (from 100 to 3000 ppm) on a Chromosorb 103 column at 30°C and 70°C. Carrier gas flow-rate, 22 cm³/min. Thermal conductivity detector.

ports the possible reaction of SO_2 with Chromosorb 101, 102, 104 and 106 [59,60]; this was found to be true at high temperatures but of minor importance at room temperature. On the other hand, very high retention times were observed for sulphur gases on acrylic polymers (Chromosorb 104, 105, 107 and 108) with respect to those of nitrogen compounds, making the simultaneous determination of these compounds impracticable. Very long retention times and peak asymmetry up to the sudden rise of the elution front followed by a near-zero slope of the peak tails, giving a step aspect to the chromatogram, were observed, making quantitative analysis unreliable. Reaction of nitrogen oxides with the polymer, resulting in sample disappearance, formation of decomposition products, yellowing of the polymer beads and changes in retention times of non-reactive compounds after the injection of large reactive samples were also observed on acrylic polymers. From a practical point of view, Chromosorb 101, 102, 103 and 106 [all styrene–divinylbenzene or polystyrene polymers with pore diameters ranging from 50 Å (type 106) to 85 Å (type 102) and 3500 Å (types 101 and 103)] were found to be suitable for the routine analysis of samples containing both sulphur and nitrogen gases. Peak asymmetry was observed for some compounds on these stationary phases at high concentrations of samples (see Figs. 1–3). Therefore, the retention values were measured by

injecting very small amounts of tail-forming compounds, in order to operate in a reasonably linear region of the partition isotherm.

Tables I and II show the retention times, t'_R (adjusted with respect to the elution time of hydrogen coincident under these conditions with that of the helium carrier gas), and the retention index values measured on these columns at different temperatures. Figs. 4 and 5 show the linear changes in the retention index values as a function of the reciprocal of absolute column temperature. The correlation
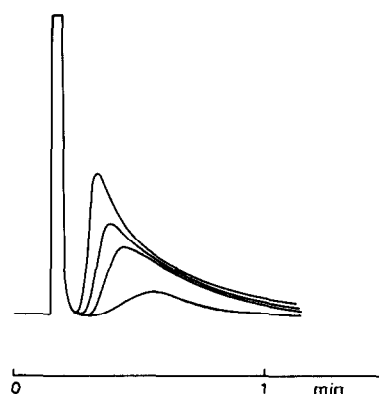

Fig. 2. Asymmetry of NO₂ peak at various concentrations (from 100 to 500 ppm) on a Chromosorb 106 column at 30°C. Carrier gas flow-rate, 22 cm³/min. Thermal conductivity detector.
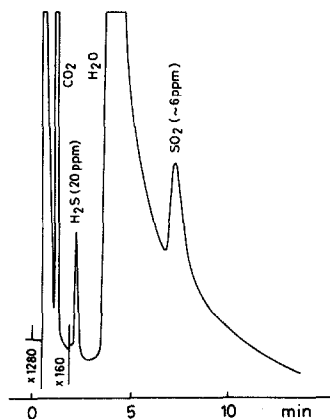
Fig. 3. Asymmetry of water peak and its interference with SO_2. Analysis of sulphur-polluted exhaust gases from a chemical plant. Helium detector; carrier gas flow-rate, 22 cm³/min; temperature, 100°C; sample amount, 0.5 cm³.

coefficients, calculated at five temperatures for compounds whose analysis can be carried out in the range 30–100°C, and at three temperatures for compounds that require the range 70–100°C, were better than 0.98 for all of the compounds, except

H_2O, NH_3 and SO_2, for which unsymmetrical peaks led to uncertainty in the retention times at the lowest temperatures and to correlation coefficients depending on the column and ranging between 0.90 and 0.96.

Different slopes for different compounds were observed, leading to peak coincidence at some temperatures and to elution order inversions. Changes of the I values as a function of polymer batch or column ageing were observed for polar compounds, mainly H_2O and NH_3. The graph for Chromosorb 101 in Fig. 1 shows with near parallel lines the minimum, the average and the maximum values observed for these compounds during the experiments. Average values are given in Tables I and II.

The most suitable column for the separation of a given gas mixture can be selected on the basis of the reported values and graphs. Generally, severe interference of the H_2O peak with SO_2, NH_3 and COS was observed with wet samples, and inversion of the elution order of the pairs N_2O–NO and C_2H_2–C_2H_4 with temperature took place on some columns. The previously observed dependence of retention times

TABLE I

ADJUSTED RETENTION TIMES, t'_R (min), AND RETENTION INDICES, I, ON CHROMOSORB 101 AND 102 COLUMNS AT VARIOUS TEMPERATURES

Gas	Chromosorb 101				Chromosorb 102					
	30°C		70°C		30°C		70°C		100°C	
	t'_R	I	t'_R	I	t'_R	I	t'_R	I	t'_R	I
CH_4	0.41	100	0.30	100	0.71	100	0.38	100	0.27	100
C_2H_2	4.13	192	1.26	194	6.75	189	2.29	184	1.10	181
C_2H_4	3.45	184	1.11	186	7.43	193	2.39	186	1.13	182
C_2H_6	5.09	200	1.37	200	8.96	200	3.18	200	1.54	200
C_3H_8	36.41	300	6.11	300	76.94	300	14.35	300	5.46	300
CO_2	1.64	155	0.60	145	2.78	154	1.17	152	0.63	149
COS	21.15	272	4.81	284	38.92	268	8.99	269	3.70	269
H_2S	12.21	244	3.63	265	21.09	240	5.49	236	2.35	233
SO_2	58.38	324	8.81	324			13.63	297	7.85	329
NH_3[a]	12.77	247	4.48	279			11.86	287	7.38	324
N_2O	2.45	171	0.98	178	3.61	164	1.53	165	0.85	166
NO	2.57	173	0.88	171	4.84	176	1.25	156	0.57	143
NO_2	1.72	157	0.64	150	3.39	161	0.95	143	0.45	130
H_2O[a]	25.89	283	6.72	306			10.64	280	7.25	322

[a] For NH_3 and H_2O average values are given (see text).

TABLE II

ADJUSTED RETENTION TIMES, t_R' (min), AND RETENTION INDICES, I, ON CHROMOSORB 103 AND 106 COLUMNS AT VARIOUS TEMPERATURES

| Gas | Chromosorb 103 | | | | | | Chromosorb 106 | | | | | |
| | 30°C | | 70°C | | 100°C | | 30°C | | 70°C | | 100°C | |
	t_R'	I	t_R'	I	t_R'	I	t_R'	I	t_R'	I	t_R'	I
CH_4	0.35	100	0.28	100	0.14	100	1.76	100	0.83	100	0.54	100
C_2H_2	3.91	195	1.08	200	0.46	204	18.11	185	5.25	183	2.68	181
C_2H_4	3.17	187	0.87	184	0.37	186	17.04	183	5.39	184	2.88	185
C_2H_6	4.39	200	1.07	200	0.44	200	27.7	200	7.70	200	3.91	200
C_3H_8	23.97	300	4.04	300	1.41	300			39.56	300	15.80	300
CO_2	1.59	160	0.54	149	0.22	141	6.84	150	2.49	149	1.42	149
COS	18.25	284	3.65	292	1.38	298			21.93	264	8.18	253
H_2S	12.43	261	3.64	292	1.67	315	41.60	216	10.93	221	5.69	227
SO_2	3.40	190	1.55	228	1.05	274			21.50	263	9.04	260
NH_3[a]	13.94	268	4.12	301	1.88	325			17.80	251	6.59	237
N_2O	2.77	174	1.07	200	0.55	219	9.66	162	3.35	162	1.87	163
NO	2.20	172	0.71	169	0.20	166	6.89	150	2.52	151	1.49	151
NO_2	0.53	116	0.34	114	0.16	113	1.14	84	0.82	99	0.50	105
H_2O[a]	18.30	284	4.32	305	1.78	320			19.3	256	9.09	260

[a] For NH_3 and H_2O average values are given (see text).

on polymer batch and column ageing [51,61] may give different results under other experimental conditions. This may change the temperature where the retention times of compounds showing inversion of

Fig. 4. Retention indices on Chromosorb 101 and 102 at different temperatures. On Chromosorb 101 the maximum, average and minimum values for H_2O and NH_3 are given.

elution order are coincident. Moreover, as the peak widths depend on the column length and efficiency and, for low concentrations, on the volume of sample injected to permit good sensitivity, a change in the temperature interval is possible before and after the crossing point where peak separation is too small. A check of the true performance of the column used with authentic samples is therefore necessary to confirm the identification when closely eluting compounds are analysed.

If the required separation cannot be obtained with any of the pure stationary phases, a tailor-made column obtained by homogeneously mixing suitable amounts of two different Chomosorb types, calculated by interpolation of the retention times or retention indices on the two pure phases, can achieve the desired result [62,63]. Mixing of different types of porous polymers is sometime precluded by electrostatic effects that glue the small beads in clusters that are difficult to pour into the column, but it was experimentally checked that Chromosorb 101, 102, 103 and 106, probably owing to their similar chemical composition, can be mixed together in any ratio. Series connection of different lengths of columns filled with pure phases is also possible, but in this
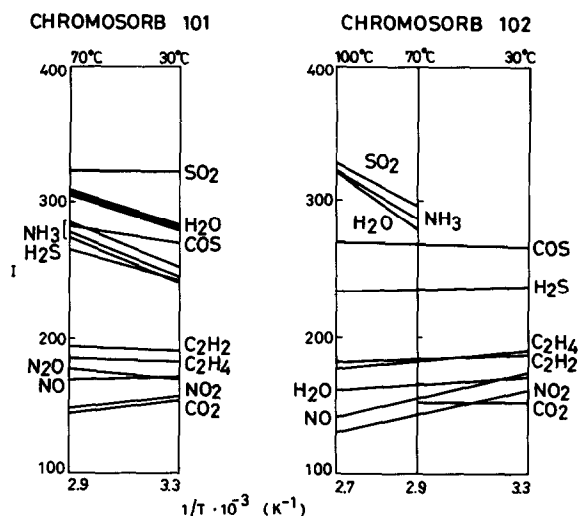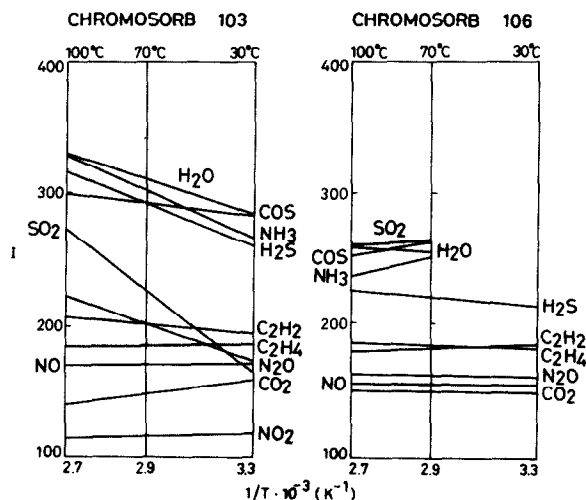
Fig. 5. Retention indices on Chromosorb 103 and 106.

Fig. 6. Effects of different phenomena on quantitative results at low concentration. S = Peak area (integration counts); Q = concentration of the component in the sample injected (ppb). Lines: (A) ideal response; (B) system contamination; (C) vacancy chromatography; (D) absorption and reaction; (E, F) area losses due to integration. For full explanation, see text.

instance the prevailing effect of the upstream column, working at higher pressure, must be taken into account in the calculation of the phase ratios.

Accuracy at low concentration

As mentioned in the Introduction, a reason for the limited application of GC to routine and automated analysis of sulphur and nitrogen gas mixtures at low concentrations is the scatter of the results, often attributed to reaction or decomposition phenomena. These effects, when present, are often negligible with respect of other causes of anomalous or reduced response. Different kinds of deviations from linearity of the plots of peak area *vs.* sample amount were observed during calibration runs extended down to low concentrations, and can be summarized and ascribed to different phenomena, illustrated in Fig. 6 with various lines plotted on a log–log scale, in order to emphasize the behaviour at low concentrations. As Fig. 6 is intended to show graphically the different behaviours connected with various phenomena, the units are not specified as they can change under different conditions and with different detectors. The data used for this plot were obtained with the helium detector and the abscissa values are therefore in the ppb range, the area values being expressed as integration counts at an electrometer range of 10^{-11} A/mV ($\times 10$ attenuation with respect of the maximum sensitivity of the system). Lines A–F in Fig. 6 can be described as follows.
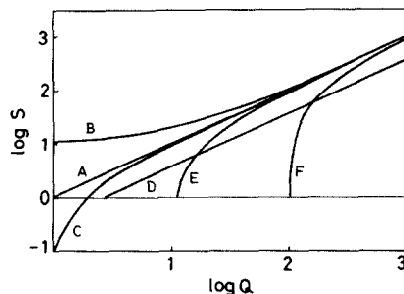
(A) Theoretical response, with area S linearly proportional to amount Q.

(B) Memory effect, when adsorbed amounts of previous samples of higher concentration are released into further less concentrated or zero samples, yielding a "blank" area value. With the samples analysed in this work, memory effects were found for sulphur gases, mainly SO_2, with glass or metal columns and connections. This effect was strongly reduced by using PTFE tubing and PTFE-lined sampling systems.

(C) Vacancy chromatography effect, due to the presence in the carrier gas of traces of the compound to be analysed. When the concentration of the sample decreases below the carrier contamination, a "plug" of contaminated carrier is replaced with a cleaner gas volume and this results in a negative peak. When the pressure in the carrier line at the sampling valve is equal to that in the sample line, no peak is observed when the concentrations of the carrier and of the sample are the same. This "zero area" point moves up and down along Q axis depending on the pressure difference between the carrier and sample streams. Vacancy chromatography phenomena were often observed when using the helium detector at high sensitivity and were strongly reduced by purification of the carrier gas and accurate checking for any possible leakage.

(D) Adsorption in the system proportional to the partial pressure of the compound in the system (*i.e.*, to the concentration in the sample). The straight line on a linear scale has a slope smaller than 1; on

a logarithmic scale as in Fig. 6 it is parallel to line A in the concentration range where the adsorption is proportional to concentration, while approximating line A at high concentrations when active adsorbing sites become saturated. With sulphur and nitrogen gases this effect was observed on polar Chromosorb types.

Important reasons for the deviation from linearity are not connected with the chromatographic system (injector, column, stationary phase, detector) but depend on the electronic procedures used for peak area integration. The peak detection algorithms of currently used data systems are activated by the increase in the first derivative of the signal (*i.e.*, by its slope) as a function of time. Narrow and symmetrical peaks are detected early and the integrated area closely approximates the true value. Large and tailing peaks, characteristic of NH_3, H_2O and SO_2, are detected later, when their slope changes appreciably with respect of that of the baseline. Some integrators can partially compensate for the delayed peak detection by re-examining some "bunches" of data, collected before the peak detection point, until a zero difference between contiguous values, *i.e.*, a baseline condition, is found. This correction fails, or is less efficient, on the peak tail, and therefore non-symmetrical peaks are more prone to "area loss" than symmetrical peaks. By decreasing the amount of sample, flatter peaks with smaller initial and final slopes are formed, and appreciable deviation from linearity are observed. Referring to Fig. 6, two curves were found as follows.

(E) Integration area losses at low concentration with symmetrical peaks, when the integration defect is due only to the delay of the slope sensitivity system in detecting the start and end of peaks having the same slope.

(F) Integration area losses at low concentration with non-symmetrical or tailing peaks, when the slope at the peak end is much smaller than at the peak start.

Plots E and F in Fig. 6 were obtained by standard integration programs that automatically increase the slope sensitivity when the width of a detected peak is 50% greater than that of the previous peak. This system often fails to detect peaks having a shape different from that of others previously appearing in the chromatogram. Of course, by programming the slope sensitivity or peak detection

parameters as a function of retention time or, better, by adjusting these values just before the elution of non-symmetrical peaks, the area loss can be substantially reduced and reasonable accuracy achieved. The results shown here seems to confirm that often the area losses responsible for inaccurate results in the determination of polar or reactive compounds are not due to decomposition or absorption in the column but depend on improper adjustment of the integration systems. At the lowest concentrations only, memory effects and vacancy chromatography may influence the quantitative results.

The minimum detectable level of each compound obviously depends on the detector used and on the occurrence or lack of vacancy or blank phenomena. As an example, the detection limit in absence of these phenomena of all the present compounds with universal detectors is in the region of 10^{-5} g with TCD and 10^{-11} g with HeD. By using flame photometric detection, the detection limit for sulphur is 10^{-9} g.

ACKNOWLEDGEMENT

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