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CONSIDERATIONS FOR THE DESIGN OF A ROTATING UNIT FOR CONTINUOUS PRODUCTION BY GAS CHROMATOGRAPHY AND ITS APPLICATIONS

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SUMMARY

An apparatus for a continuous gas chromatographic process is presented; its principles of operation have already been described by M. TARAMASSO et al.[1-6].

The main features of the process are: efficiency at least equal to that of an analytical column, possibility of obtaining several components at the same time or a single peak in many traps, with a high-grade central fraction, and feed rates up to 400 ml/h.

PRINCIPLES OF THE PROCESS

By combining a chromatographic technique with an adequate moving system it is possible to transform a substantially discontinuous process into a continuous one.

In the process described here this principle was used. Unlike SCOTT's[1] process wherein the motions are intimately connected and have opposite sense but the same direction, in this process the two factors are maintained distinct and act in orthogonal directions.

The fundamental idea and the simplest way of putting into practice the principle, may be described as follows: as shown schematically in Fig. 1, let us suppose that a column is moving in a plane at a speed v_s, with respect to the feeding and collecting systems which are stationary. The column assumes successively the positions indicated by dashed lines, whilst the carrier gas flows in the direction indicated by the arrows.

If the length of the chromatographic column is L, and the retention time of the component "i" is t_R, the distance covered by this component in the plane is given by the combination of the two speeds (v_s and L/t_R), and the elution which occurs in the position X_1 can be defined as follows:

$$X_1 = v_s \cdot t_{R1}$$

However, owing to longitudinal diffusion, the elution of the component will occur in a range ΔX_1 proportional to the band broadening Δt_{R1}.

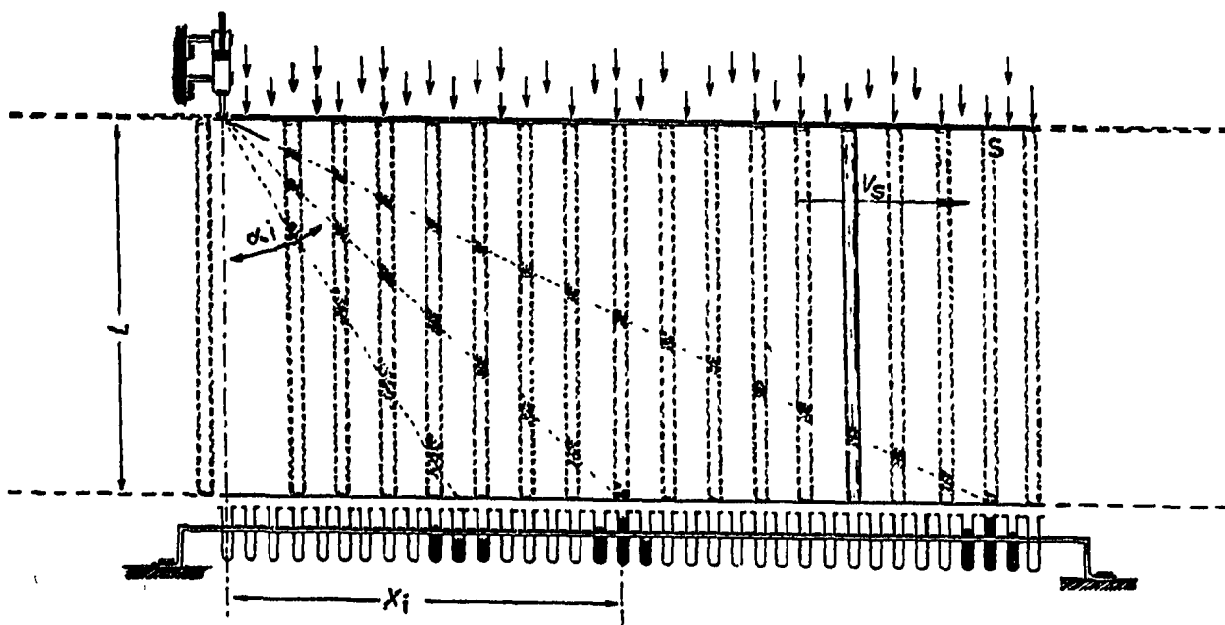If a series of columns is moved into the appropriate positions at successive

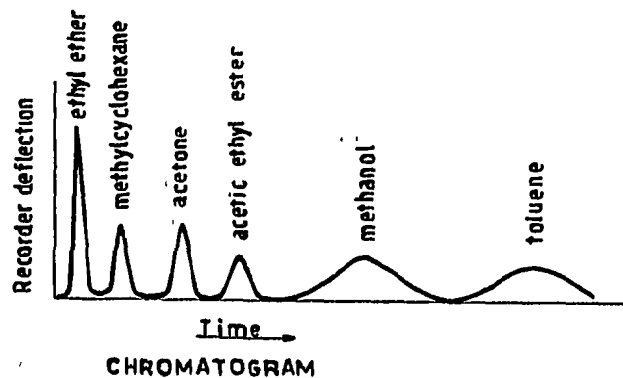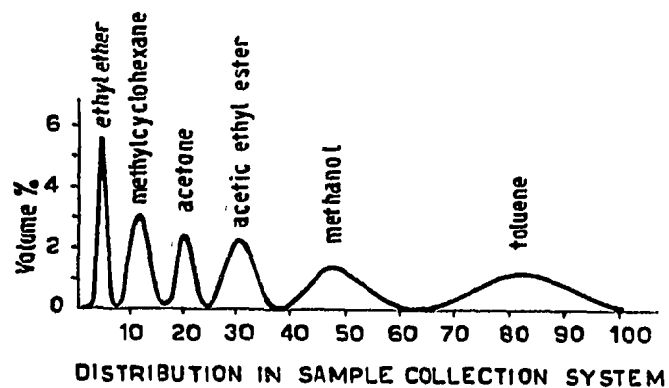Fig. 1. Schematic diagram of continuous gas chromatography.

Fig. 2. Equivalence between the chromatogram and space distribution, obtained with a six-component mixture.
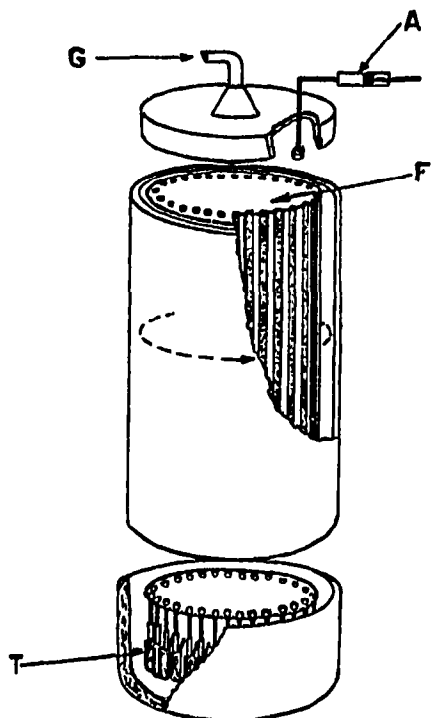
Fif. 3. Diagram of the rotating unit for preparative scale gas chromatography. G = carrier gas inlet; A = sample feeding system; F = bundle of columns, T = trapping system.

intervals, the process is made continuous: the component distribution in the trap-system is the space equivalent of the elution diagram given by a single column over a period of time (Fig. 2). Finally, if the columns are placed along the generatrices of a rotating cylinder having a radius r (Fig. 3), the process becomes really continuous and the foregoing equation becomes:

$$X_1 = 2\pi r v t_{R1}$$

Where v is the number of revolutions of the cylinder per unit of time. The conditions corresponding to the maximum utilization are obtained when the last component (retention time t_{R2}) is eluted adjacent to the first component (t_{R1}). The number of revolutions of the series of columns is given by:

$$v = \frac{1}{t_{R2} - t_{R1}}$$

ASSEMBLY AND OPERATION FEATURES OF THE APPARATUS

In our second model the number of columns forming the cluster was limited to 36, to facilitate handling and in order to ensure feed rates between 2 and 400 ml/h.

An important feature is the complete automation, thus handling the apparatus does not require skilled personnel. The cluster, consisting of 2 m long, U shaped stainless steel columns, is easily interchangeable. The cluster must be filled in such a way that the carrier gas flow rate in two adjacent columns does not differ by more

than $\pm 1\%$. Using 6 mm diameter columns, the system will have an efficiency practically equal to that of an analytical one.

As a result of the structural features of the system, the sample introduction occurs in the absence of carrier gas flow, in such a way that preliminary dilution of the sample is avoided.

As the carrier gas enters some moments after the sample, a frontal chromatographic process takes place, so the components are already partially separated when the carrier gas is let in.

The introduction of the samples is effected by a micropump, whose feed rate can be varied continuously from 2 to 400 ml/h, and which has a reproducibility of 1%. This sampling device is capable of feeding volatile liquids or viscous mixtures. The cluster of columns, the feeding system and carrier gas inlets are located in a chamber, the temperature of which may be varied from room temperature up to 220°, with a high accuracy ensured by forced air circulation. The speed of rotation of the cluster can be adjusted continuously from 1 to 9 revolutions/h.

For preparative purposes the criteria for the selection of the stationary phase differ considerably from those valid for analytical gas chromatography. This is particularly true when the separation of a single substance from a complex mixture is required. In this case it is more convenient to elute the components which are not required all together. An example of this is the separation of benzene from all the other hydrocarbons in a cut of petroleum boiling in the range 65–95°; this is shown in Fig. 4. When such a selective stationary phase is not available, one can resort to a mechanical artifice to achieve the same purpose. By suitable selection of the operating conditions, it is possible to allow the tail impurities to elute so that they overlap into the head impurities. This device has been used in the separation of 3-methylpentane from the distillation heads of n-hexane. The analytical chromatogram is shown in
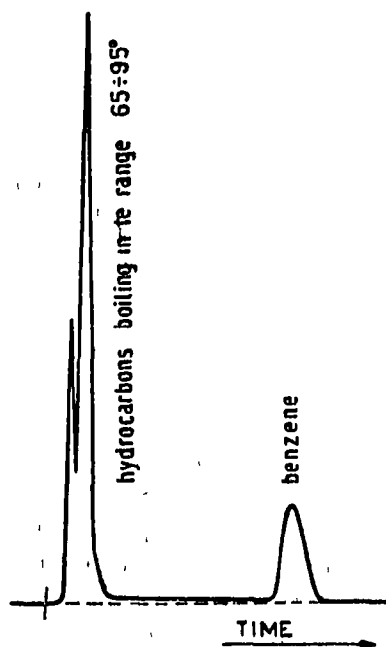

Fig. 4. Separation of benzene from hydrocarbons boiling in the range 65–95°.
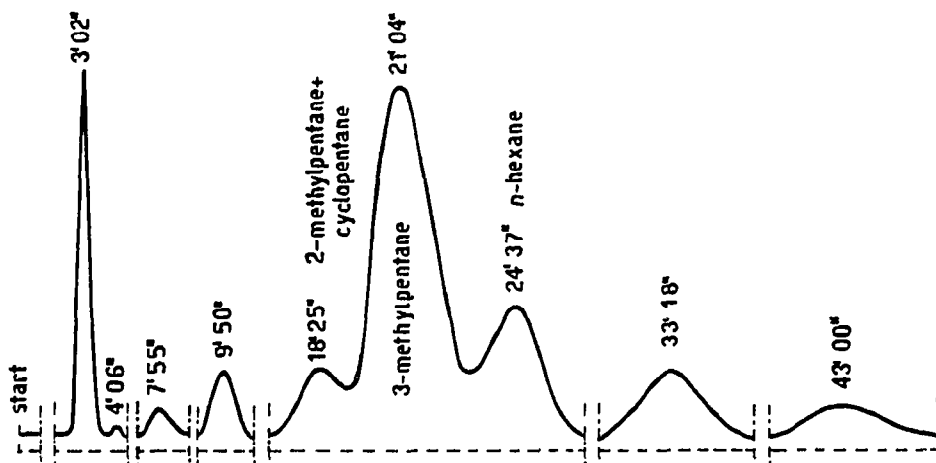
Fig. 5. Chromatogram of the "tops of *n*-hexane distillation".

Fig. 5; Fig. 6 shows the hypothetical chromatogram which the apparatus has been compelled to produce.

Fig. 7, which shows the purity *versus* collecting position, clearly indicates that, while the initial and ultimate fractions collected contain impurities, high purity 3-methylpentane is obtained in the central traps. The same example shows the exceptional purity obtainable by this process: percentages of 99.9% and 99.99% should be considered normal for the central portion of each peak.

FACTORS REGULATING THE PERFORMANCE OF THE APPARATUS

The quantity of a mixture which can be treated per unit of time depends on the number of the columns composing the cluster (*N*), on the maximum quantity of
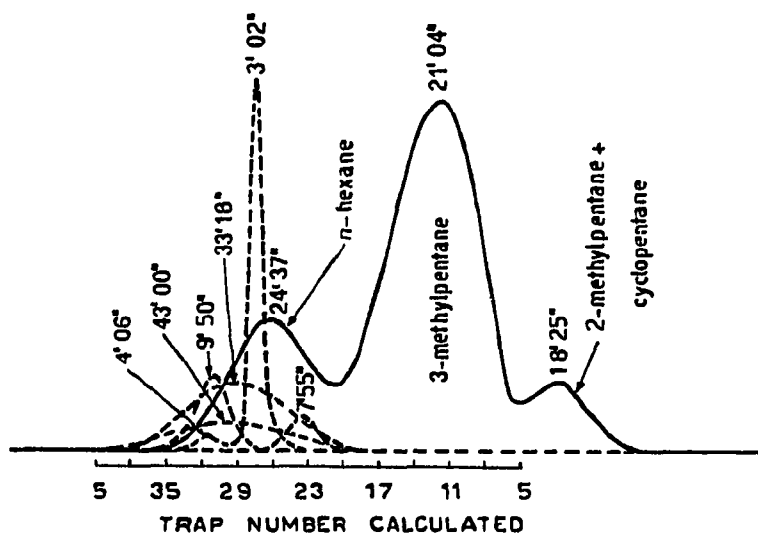

Fig. 6. Apparatus program for the separation of 3-methylpentane.

sample that can be injected into each column for obtaining the desired purity (q_m), and on the number of the rotations of the cluster per unit of time:

$$Q = N \cdot q_m \, \nu$$

Thus, the maximum quantity that can be injected to obtain the desired degree of purity depends on the resolution R of the two key components, which by definition is expressed as follows:

$$R = 2 \, \frac{t_{R2} - t_{R1}}{W_{b1} + W_{b2}} \simeq 2 \, \frac{\Delta t}{\Delta W_b}$$

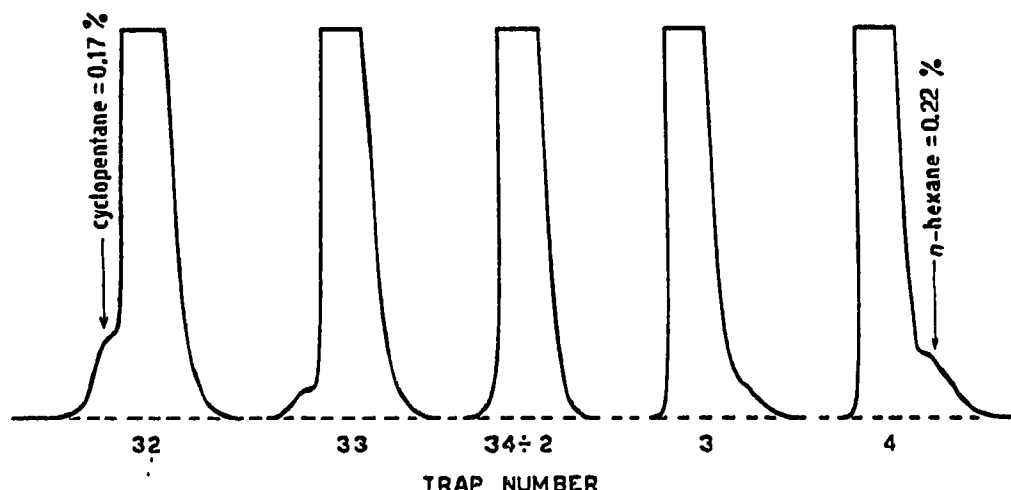where W_b is the width of the peak base for the component eluting last.

Fig. 7. 3-Methylpentane distribution in the trapping system.

In order to limit the width of the peak, and at the same time obtain high values of q, it is necessary that the variable t has as small a value as possible. Therefore the optimization of q requires a compromise between these two antithetical factors (maximum value of $t_{R2} - t_{R1}$ and minimum value of t_{R2}) since the former is an increasing function of the latter.

On the other hand, a low retention time of the component 2 allows a high revolution rate of the cluster and minimum use of stationary phase per unit weight of separated product.

In practice short columns are preferred ($1 \text{ m} < L < 3 \text{ m}$) and the stationary phase, temperature and flow rate of the carrier gas would be selected so as to obtain low retention times and, at the same time, a satisfactory resolution of the components. The optimization of the above mentioned factors is effected in a preliminary study, defined programming, where the same experiments are made on a "pilot" chromatographic column identical to those forming the cluster and mounted on an analytical chromatograph.

The program makes the process independent of the need to use a detector or any other device to record the eluent peaks.

APPLICATIONS

The method described is primarily applicable to the separation of mixtures which cannot be otherwise easily treated, such as azeotropes, isomers, close boiling point substances.

As an example, it has been possible to separate the *cis-trans* isomers of pentene-2 by means of a diethylene glycol and silver nitrate stationary phase at 30° with a feed rate of 60 ml/h. This is equivalent to a capacity of 1.3 l/day per kg of packing with a consumption of 0.85 m³ nitrogen. Such a potentiality shows that if the process was applied on a large scale it would be economic. The purity of the *cis–trans* isomers separated was 99.6%. A purity higher than 99.99% has been obtained in the refining of isoprene from a mixture containing the required product mixed with 90% methyl-butenes as the main impurities. In this case a production rate of 20 l/week was maintained for three months without any band shifting or other inconvenience.

The feed rate is reduced according to the relative volatility of the components to be separated and to the complexity of the mixture.

An example of a rather difficult separation is that of the methallylchloride from isocrotyl chloride. The starting mixture also contained small amounts of *tert.*-butyl chloride and isobutylene. With a delivery of 21.6 ml/h samples of methallylchloride, 99.99% purity, and isocrotyl chloride, 99.87% purity, have been obtained. Fig. 8
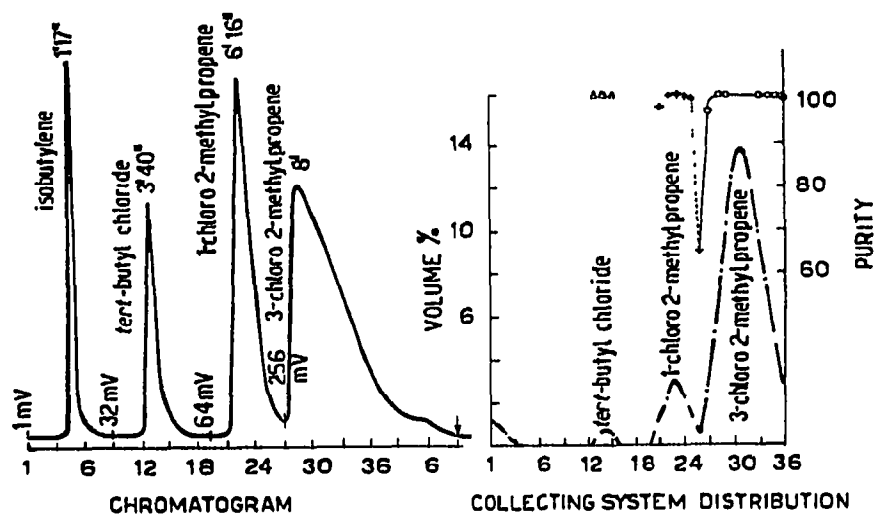

Fig. 8. Chromatogram and collecting system distribution, in the separation of 3-chloro-2-methyl-propene and 1-chloro-2-methylpropene.

shows the chromatogram used for programming the apparatus and the distribution obtained in the collecting system, using Carbowax 400 as stationary phase and working at 90°.

The high efficiency of this type of column equalling that of an analytical system is utilized in the following difficult separation, shown in Fig. 9. A separation of the *cis–trans* isomers of piperylene was carried out starting from a trade product having the following composition:
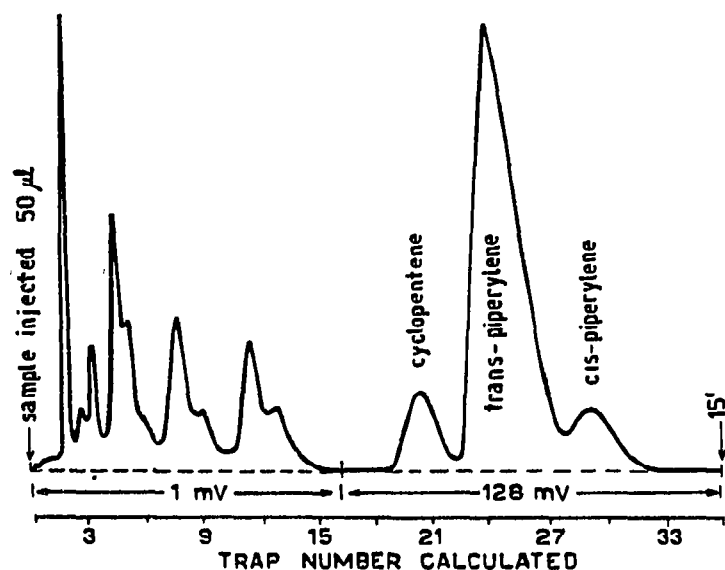
Fig. 9. Program for the separation of cis–trans piperylene.

Light impurities	0.31%
Isoprene	0.76%
Cyclopentene	9.28%
trans-Piperylene	79.27%
cis-Piperylene	10.38%
Cyclopentadiene	(0.007%)

1,2-Bis(2-cyanoethoxy)-ethane was found to be a suitable stationary phase for this mixture. The rotating unit was run with a feed rate of 7.2 ml/h. The distribution obtained in the collecting system was equivalent to that of the chromatogram (Fig. 9) and the purity of the trans-piperylene fraction collected was 99.9% ; the cis fraction obtained had a purity of 81.9% with 18.0% of trans isomer, after treatment with maleic anhydride it gave a product of 99.9% purity. The recovery of these volatile compounds, made with dry ice and Dowanol was about 70% by vol. based on the feed.

Mixtures of terpenes (namely camphene, myrcene, and α,β-pinenes), which present similar difficulties, have been separated on Carbowax 400 at 104° with a feed rate of 10 ml/h ; purities of 99.8–99.9% for single components, and in some cases even higher than 99.99%, have been obtained.

The applicability of the method is far from being limited to the examples cited above. The high feed rates possible, the very high purities obtainable and the compactness of the apparatus render the method an effective alternative to the fractional distillation. Proof of this was given by the separation of iso- and n-pentane the result of which was very competitive as far as the delivery and purity realized were concerned when compared to the fractionation obtainable with an 85 plates Oldershaw column. For the reasons mentioned, the prospects for producing hydrocarbons of very high purity are remarkable. In addition to the 3-methylpentane already mentioned, cyclopentane has been obtained from the bottoms of an n-pentane distillation in a similar way by using a stationary phase of 1,2-bis(2-cyanoethoxy)-ethane at 39° with a feed rate of 45 ml/h. The purification of n-hexane of 95% purity was effected

with a feed rate of 30 ml/h; a final product of 99.99% purity was obtained. In a purification of cyclohexane we obtained a product whose chromatogram showed no impurity traces.

A special feature of the process is the possibility of obtaining a number of components from a mixture simultaneously. This is shown by the separation of reaction crudes, which normally require a long fractionation procedure and separation analysis.

1,1-Dichloro-2-vinylcyclopropane and 4-vinylcyclohexene-1 with purities of 99.9% have been obtained from the mixture resulting from the reaction between sodium trichloroacetate and butadiene. The feed rate in this case was 30 ml/h.

The reaction mixture between cyclopentadiene and isoprene was fed into the apparatus at a rate of 4 ml/h at 110° and in a single working step 1,4-dimethyl-1-vinylcyclohexene-3, limonene and methyltetrahydroindene were separated with a purity of 99.9% for each component.

We could separate the dihydrodicyclopentadiene with a purity higher than 99.9% from a mixture of hydrogenation products of the dicyclopentadiene, with a rate of 6 ml/h at 140° and a stationary phase of methylsilicone polymer.

The various features of the preparative rotary chromatograph and its possible applications render it a valuable tool for laboratory research, and for small scale industrial production.

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