Determination of Acrolein in Air as an Oxazolidine Derivative by Gas Chromatography

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Acrolein in air (0.13 to 1.5 mg/m^3) reacted with 10% (w/w) 2-(hydroxymethyl)piperidine coated on XAD-2 (16/50 mesh) sorbent to produce a bicyclic oxazolidine, 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane. This compound was desorbed from the sorbent with toluene and determined by gas chromatography with nitrogen-specific detection. Separation of this oxazolidine from the oxazolidines of formaldehyde and acetaldehyde was accomplished by use of a 2 m × 4 mm i.d. column packed with 5% SP-2401-DB on Supelcoport. Sorbent tube samples were collected at a rate of 100 cm^3/min for up to 8 h and found to be stable for at least 4 weeks at room temperature. Overall relative standard deviation for the sampling and analytical method over this range was 11.1%.

Acrolein is a widely used industrial chemical which can cause irritation of the eyes and respiratory tract. Because of these properties, the Occupational Safety and Health Administration has established a Permissible Exposure Limit (PEL) of 0.1 ppm (0.25 mg/m^3) (*1*). With this low exposure limit and the reactive nature of acrolein, many of the methods developed for the monitoring of this compound have major shortcomings when used for personal samples. These shortcomings include limited sample volume (*2*, *3*), required storage of samples at 0 °C (*2–5*), less than quantitative recovery (*3*), cumbersome sampling train (*4*, *5*), and use of toxic chemicals in the sampler (*4*, *5*). Because of the limitations of the existing methodology for acrolein, the need for an improved personal sampling and analytical method was indicated.

Previous work in our laboratory on formaldehyde (*6*) has demonstrated the utility of a reagent-coated sampling medium. This approach seemed to overcome sample instability problems with this compound. Since sample instability was a major problem with acrolein, a similar approach via derivatization on a reagent-coated sorbent was attempted. It was believed that this approach would also eliminate the small sample size required by previous methods, since once the compound had reacted with the coating, its volatility and reactivity would be greatly reduced.

EXPERIMENTAL SECTION

Reagents. Acrolein was obtained from Matheson, Coleman and Bell and distilled before use to remove the stabilizer (0.25% hydroquinone, 98%+ purity as determined by GC). A solution of known acrolein concentration was prepared by addition of 10 μg (11.9 μL) of distilled acrolein via a 10-μL syringe to 10 mL of toluene. This solution was used for the spiking experiments and for standards preparation. Toluene, chloroform, isooctane, methanol, acetone, and methylene chloride were Burdick and Jackson solvents distilled in glass. 2-(Hydroxymethyl)piperidine, 2-(benzylamino)-1-propanol, 1-(benzylamino)-2-propanol, and 2-(benzylamino)ethanol (BAE) were obtained from Aldrich Chemical Co. 2-(Hydroxymethyl)piperidine was recrystallized from isooctane four to five times before use (mp 68–70 °C) to remove impurities present in the technical grade material (93% purity). Amberlite XAD-2 (16/50 mesh) was obtained from Supelco, Inc., and Rohm and Haas Chemical Co. The sorbent was extracted with a 50:50 acetone–methylene chloride solution in a Soxhlet extractor for 4 h (ca. 30 min cycle time) and then dried under 1 mmHg vacuum overnight.

Apparatus. Critical orifices made by Langer Jewel Bearing Plant, Rolla, ND, (nominal 100 and 200 cm^3/min) were used in conjunction with the laboratory vacuum system (432 mmHg) for all sampling.

Air and nitrogen flow in the vapor generator was measured and controlled with mass flow controllers from Navtec (dual controllers, 100 standard cm^3/min) and Tylan (Model RO-14-100, 20 standard L/min). Humidity in the generation system was generated by passing dry air over a heated water bath and was measured with a Hydrocon Precision electrohumidity reader-controller. This controller system has a solenoid which was connected to the water bath heater and provided control of the humidity to ±10%.

A Varian Model 3700 gas chromatograph equipped with a packed column injection system and a thermionic specific detector (nitrogen specific) was used for sample analysis. Samples were injected with a Varian Model 8000 autosampler. The column used for analysis was a 5% SP-2401-DB on Supelcoport (100/120 mesh) packed glass column (2 m by 4 mm i.d.). Injector and detector temperatures were 230 °C and 250 °C, respectively. The initial column temperature was held at 90 °C for 8 min, and the temperature raised at 20 °C/min to 200 °C and held for 13 min. Helium at 30 cm^3/min was used as the carrier gas.

Mass spectral data were obtained on a V.G. Micromass 7070HS mass spectrometer (70 eV electron impact spectra) interfaced with a Hewlett-Packard 5840 gas chromatograph, equipped with a 25 m × 0.2 mm i.d. fused silica Carbowax 20M capillary column.

Infrared spectral data were obtained on a Perkin-Elmer Model 283 infrared spectrometer. Sodium chloride cells (0.1 mm) were used.

Preparation of the Sampling Devices. To 9 g of XAD-2 (16/50 mesh) was added 1 g of purified 2-(hydroxymethyl)-piperidine in 50 mL of toluene. This slurry was allowed to sit for approximately an hour with occasional swirling. The toluene was removed at reduced pressure by rotary evaporation at ca. 40 °C and the sorbent dried at 1 mmHg vacuum for 1 h. The dried coated sorbent was packed into soft glass tubes, 10 cm × 4 mm i.d. Each tube contained a 120-mg front section and a 60-mg backup section of the coated sorbent. The two sections were retained and separated by small plugs of silanized glass wool.

Acrolein and Acetaldehyde Generation. Acrolein samples were collected in the laboratory with the generator shown in Figure 1. House air which had been dried and scrubbed of carbon dioxide and organics was humidified (80% relative humidity) as described previously and metered into the generator. Acrolein vapor was generated with a glass diffusion tube (0.1 cm i.d. by 17 cm in length) filled with acrolein. Dry nitrogen swept the acrolein vapor from the diffusion tube maintained at 10 °C in a constant temperature bath (Lauda Model K-4/R) into the mixing flask of the generator. Dilution air was metered into the mixing flask with a mass flow controller at rates between 5 and 22 L/min to provide dilution of the contaminants generated. Mixing was accomplished by the turbulent flow of the dilution air through the mixing flask. The generated concentration of acrolein was determined independently using a modification of NIOSH method P&CAM 211 (*4*) developed by Shell Development Co. (*5*). The modifications were a change in heating bath temperature from 100 °C to 70 °C, an increase in immersion time in the heating bath from 5 min to 30–35 min, and the inclusion of a cooling step (5 min in an ice bath) for the samples after heating.

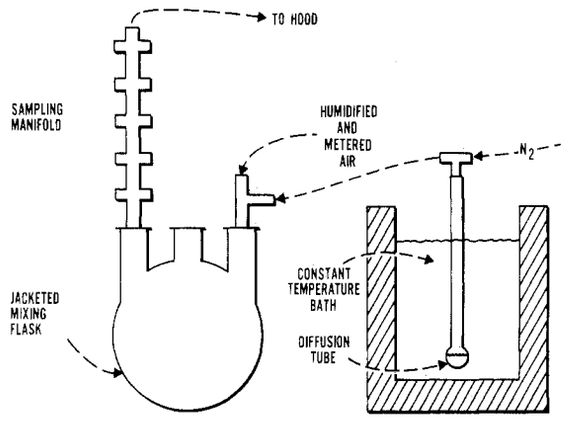

Figure 1. Diagram of sample generation system.

Acetaldehyde was generated in a similar fashion using a glass diffusion tube. For the low level stability study with acrolein, acetaldehyde was generated as a cocontaminant by attaching the acetaldehyde diffusion tube downstream of the acrolein diffusion tube. The concentration of acetaldehyde in the generator was determined by using the method of Beasley et al. (7) for acetaldehyde.

Tube samples were collected at the ports of a ten-port glass sampling manifold using critical orifices. All generator lines were wrapped with heating tape to prevent condensation of water and provide temperature control during sampling, since the temperature of the laboratory fume hood where the generator was placed varied from day to day. Temperature was maintained at 25 ± 5 °C for all generated concentrations.

Oxazolidine Synthesis. Approximately 1.1 mmol of aldehyde in 20 mL of toluene was added dropwise to 1.0 mmol of 2-(hydroxymethyl)piperidine in 30 mL of toluene. The solution was stirred for 4 h and the solvent then removed by rotary evaporation. The resulting oil was then subjected to high vacuum (1 mmHg) to remove the last traces of solvent and excess aldehyde. Oxazolidine structures were confirmed with high-resolution gas chromatography/mass spectrometry using the exact mass technique (6).

Mass spectral data for the reaction product of acrolein and 2-(hydroxymethyl)piperidine (9-vinyl-1-aza-8-oxabicyclo[4.3.0]-nonane) are as follows: m/e with relative intensities in parentheses, 154 (5%), 126 (100%), 110 (6%), 102 (3%), 98 (17%), 96 (5%), 69 (13%), 57 (21%), 56 (7%), 55 (9%), 54 (5%); exact mass data, $C_9H_{16}NO$ (M + H), 154.1209 observed, 154.1231 calculated; $C_7H_{12}NO$ (M - C_2H_3), 126.0869 observed, 126.0918 calculated.

Mass spectral data for the reaction product of formaldehyde and 2-(hydroxymethyl)piperidine are as follows: m/e with relative intensity in parentheses, 127 (26%), 126 (41%), 97 (100%), 96 (23%), 69 (54%), 57 (5%), 56 (17%), 55 (24%), 54 (12%); exact mass data, $C_7H_{13}NO$ (M), 127.0990 observed, 127.0996 calculated; $C_7H_{12}NO$ (M - H), 126.0920 observed, 126.0918 calculated.

Mass spectral data for the reaction product of acetaldehyde and 2-(hydroxymethyl)pyridine are as follows: m/e with relative intensity in parentheses, 140 (6%), 126 (33%), 96 (6%), 76 (36%), 69 (100%), 56 (4%), 55 (6%), 54 (4%); exact mass data, $C_8H_{14}NO$ (M - H), 140.1109 observed, 140.1075 calculated; $C_7H_{12}NO$ (M - CH_3), 126.0911 observed, 126.0918 calculated.

Analysis. The backup section of the sampling tube and its rear glass wool plug were transferred to a 4-mL vial. The front section of the tube and the remaining two glass wool plugs were transferred to a separate 4-mL vial. Two milliliters of toluene were added to each vial. The vial was capped and placed in an ultrasonic bath for 30 min for desorption. The samples were then analyzed by injection of 1-μL aliquots of each sample into the gas chromatograph.

Calibration was accomplished by injection of standards of the oxazolidine into the gas chromatograph and plotting peak area or height vs. amount. These standards were prepared in several different ways. The first technique involved the preparation of solutions of acrolein in toluene (1 μg/μL) and 2-(hydroxymethyl)piperidine in toluene (5 mg/mL). Aliquots (2–25 μL) of the acrolein solution were added to 2-mL portions of the 2-(hydroxymethyl)pyridine solution. These standards were allowed to stand overnight to ensure complete reaction of the 2-(hydroxymethyl)piperidine with the acrolein and then analyzed by gas chromatography.

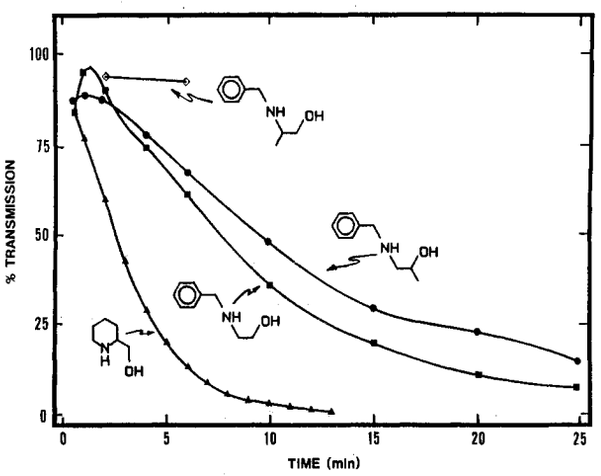

Figure 2. Infrared spectroscopy study of the reaction of acrolein with ethanolamines vs. time: (■) 2-(benzylamino)-1-ethanol; (▲) 2-(hydroxymethyl)piperidine; (◊) 2-(benzylamino)-1-propanol; (●) 1-(benzylamino)-2-propanol.

When this method was used, it was necessary to spike sorbent tubes with aliquots of the acrolein solution, allow them to stand overnight, and desorb and analyze them by gas chromatography. These samples were used to check the recovery of the acrolein from the sorbent to ensure that there was no irreversible adsorption taking place. In all instances the recovery of acrolein for the sorbent was greater than 95% when compared to the liquid standards described previously.

The second technique for preparing standards involved the spiking of 120-mg portions of coated sorbent with known amounts (2–25 μg) of acrolein. These portions of sorbent were allowed to sit overnight, desorbed with 2 mL of toluene, and analyzed by gas chromatography. The peak response vs. acrolein amount spiked was plotted for the calibration graph. With this procedure no recovery efficiency correction as described above was required.

RESULTS AND DISCUSSION

In attempts to apply previously developed methodology for formaldehyde to other aldehydes, the reaction of 2-(benzylamino)ethanol with acrolein did not yield promising results. The reaction mixture from these two compounds was a viscous oil which darkened on standing and attempts at analysis by capillary column gas chromatography did not resolve the peaks due to the oxazolidine and the 2-(benzylamino)ethanol. Since this reagent was not suitable for acrolein sampling, several other related compounds were investigated. These were 1-(benzylamino)-2-propanol, 2-(benzylamino)-1-propanol, and 2-(hydroxymethyl)piperidine. The compounds were evaluated as trapping reagents for acrolein by monitoring the reaction of acrolein with each ethanolamine by infrared spectroscopy. Chloroform solutions of each of the trapping compounds and of acrolein were prepared. The percent transmission of the initial acrolein carbonyl stretch at 1700 cm^{-1} was recorded and an aliquot of the ethanolamine under study in solution added. The decay of the percent transmission of the carbonyl absorption was monitored with time for each compound and was plotted in Figure 2. Duplicate runs were made with all compounds and the decay times averaged. It was found that of all the compounds evaluated, 2-(hydroxymethyl)piperidine reacted most quickly with the acrolein.

The reaction mixture of 2-(hydroxymethyl)piperidine and acrolein was subjected to high-resolution gas chromatographic/mass spectrometric analysis. The corresponding oxazolidines due to acetaldehyde and formaldehyde were found in the mixture and corresponded to concentrations of

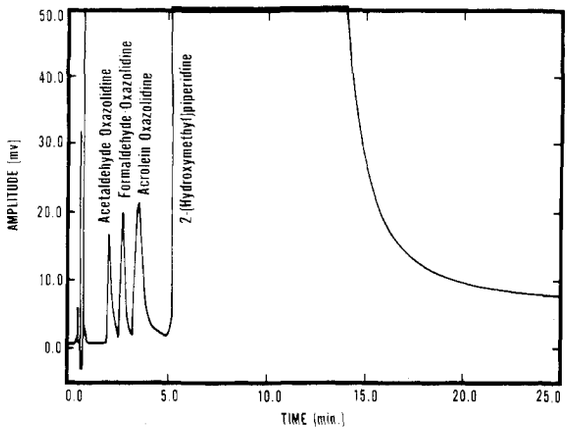

Figure 3. Packed column (5% SP-2401-DB on Supelcoport) chromatogram of oxazolidines of acetaldehyde, formaldehyde, and acrolein. *Chromatographic conditions:* injector, 230 °C; detector, nitrogen specific, 250 °C; oven, 90 °C initial hold for 8 min, program to 200 °C at 20 °C/min; flow, 30 cm^3/min helium.

approximately 1% by weight. This finding was not unusual since contamination of acrolein with acetaldehyde and formaldehyde has been reported (*8*).

Since XAD-2 (16/50 mesh), with its the large surface area (ca. 200 m^2/g), worked well with the 2-(benzylamino)ethanol coating for formaldehyde (*4*), this sorbent was used for coating with the 2-(hydroxymethyl)piperidine. To check for coating stability, a stream of dry nitrogen was allowed to flow through a tube packed with 150 mg of 2-(hydroxymethyl)piperidine coated XAD-2 sorbent at 100 cm^3/min for 4 h. The effluent from the tube was bubbled through a pair of bubblers filled with toluene. The toluene solutions were found to contain no 2-(hydroxymethyl)piperidine after the 4-h sampling period when analyzed by gas chromatography, so the coating was assumed not to volatilize from the sorbent. The minimum amount of 2-(hydroxymethyl)piperidine in toluene which could be detected with this technique was approximately 1.7% of the amount coated on the sorbent (200 μg/impinger).

After investigating several different gas chromatography columns, separation of the 2-(hydroxymethyl)piperidine–oxazolidines of formaldehyde, acetaldehyde, and acrolein was accomplished on a 2-m glass 5% SP-2401-DB on Supelcoport (100–120 mesh) packed glass column (2 mm i.d.) (Figure 3). When flame ionization detection was used, a limit of detection of 13 ng was obtained for acrolein, using a 1-μL injection volume. To analyze acrolein samples below the 0.25 mg/m^3 level, a limit of detection of at least 6 ng was needed for a 48-L sample. In order to obtain the necessary sensitivity for the acrolein analysis, a nitrogen-selective detector was used instead of a flame ionization detector. This detector also lessened solvent interference.

Attempts to synthesize the 2-(hydroxymethyl)piperidine–oxazolidine derivative of acrolein yielded crystals which were contaminated with the formaldehyde and acetaldehyde oxazolidine derivatives as determined by gas chromatographic analysis. Recrystallization of the product did not improve purity and seemed to increase the amounts of the oxazolidines due to formaldehyde and acetaldehyde present in the crystals. Since the pure oxazolidine of acrolein could not be isolated, standards for quantitation were prepared by adding known amounts of acrolein in toluene to 120-mg portions of coated sorbent. In order to obtain complete formation of the oxazolidine, it was necessary to let the sorbent sit overnight before analysis. The length of time required for complete reaction was determined by analyzing solutions of 2-(hydroxymethyl)piperidine and acrolein over 12 h by gas chromatography. It was found that height of the oxazolidine peak was at a maximum after a 12-h reaction period and remained constant for at least 3 days when stored at room temperature. Storage of desorbed samples in a refrigerator caused decomposition of the oxazolidine, possibly due to the condensation of water in the sample. By preparing standards in this manner and using them to prepare a calibration curve, we made no desorption efficiency correction on unknown samples, since it was built into the curve. A possible explanation for this 12-h reaction period is that the reaction of acrolein with 2-(hydroxymethyl)piperidine seems to be a two-step process and involves the loss of a molecule of water from the reaction intermediate in the ring forming step. In nonaqueous solution this loss of water may be a rate-limiting step.

To ensure that the oxazolidine was stable on the sorbent, each of 12 tubes was spiked with an aliquot of a toluene solution containing 19 μg of acrolein, corresponding to a 48-L sample of a 0.4 mg/m^3 concentration. Sets of six samples were analyzed after 1 and 7 days of storage at ambient temperature. Results (with 95% confidence intervals) indicated no statistically significant difference in recovery between one (101.2 ± 1.9%) and seven days (104.0 ± 3.7%).

In attempts to expand this method to other aldehydes, a spiking study was performed with acetaldehyde at the 2 mg per sample level. At this level there was appreciable migration of the acetaldehyde from the front section of the tube to the back after 7 days of storage. Also recovery was poor after day seven. The calculated capacity of the tube for acetaldehyde was 5 mg which was close to the spiked loading. A second study was performed using 0.5 mg of acetaldehyde. At this level recovery was much better after 7 days but migration of the acetaldehyde from the front section to the back was still a problem.

The capacity of the tubes for acrolein was tested at two different flow rates. Breakthrough was measured by exposing a series of nine tubes to the contaminated vapor in 80% relative humidity air. Individual tubes were removed from the sampling manifold at regular intervals and the front and rear sections of the tube analyzed. A second tube was attached in series on the last tube to be removed. If breakthrough had occurred during sampling, then material would have been collected on the backup section of the individual tubes or the backup tubes. The results of this study indicated no breakthrough of acrolein through the sorbent, even for sample volumes as large as 58 L and a flow rate of 100 cm^3/min when sampling an atmosphere of 4.9 mg/m^3. On the basis of the results of the stability study and the capacity study, the development of a sampling and analytical method for acrolein was possible. A sampling time of 8 h at a flow rate of 100 cm^3/min does not exceed the capacity of the sampling tube, even at concentrations as high as 4.9 mg/m^3 and relative humidity as high as 80%. The previously described problems of small sample volumes and sample instability had been overcome.

The capacity of the tubes for acetaldehyde was also tested at two different flow rates. No breakthrough of acetaldehyde was detected at a flow rate of 50 cm^3/min and a sample size of 8 L for an atmosphere of 68 mg/m^3. However, at a flow rate of 100 cm^3/min, significant breakthrough (>5%) was observed with a sample size of 5 L when sampling an atmosphere of 37.5 mg/m^3. This reduced capacity is probably due to the rate of reaction of acetaldehyde with 2-(hydroxymethyl)piperidine being much slower in comparison to the contact time of acetaldehyde in the sampling tube, resulting in a kinetically limited sampling rate. These results were not surprising since breakthrough of formaldehyde was observed with the 2-(benzylamino)ethanol coated Chromosorb 102 tube at flow rates of 100 cm^3/min (*6*). The use of the method for the sampling of acetaldehyde at its permissible exposure limit (360 mg/m^3) (*1*) was not possible without the potential of

Table I. Results of Determinations of Acrolein in Laboratory Generated Atmospheres Using the 2-(Hydroxymethyl)piperidine Coated XAD-2 Sorbent/GC Method

nominal concn,[a,c] mg/m³	concn (mg/m³) determined by[b,c]		
	analyst A	analyst B	analyst C
0.11 (10.2%)	0.14 (12.6%)	0.13 (16.0%)	
	0.13 (10.4%)		
0.29 (20.1%)	0.26 (7.4%)		0.29 (3.9%)
1.5 (6.0%)	1.5 (8.9%)		1.5 (6.6%)

[a] Determined by analyst A using independent method (*4*). [b] Average of six samples. [c] Values in parentheses are relative standard deviations.

significant sample breakthrough or sample migration.

The method was laboratory evaluated for acrolein by using an established procedure for the determination of overall method accuracy and precision (*9*). Three sets of samples were generated at three different acrolein concentrations (0.11 ± 0.03, 0.29 ± 0.14, and 1.5 ± 0.2 mg/m³ by the independent method with 95% confidence limits, based on triplicate determinations). The average recoveries with the 95% confidence limits were 127 ± 18% (17 samples), 97 ± 3% (12 samples), and 100 ± 4% (12 samples), respectively. No significant differences were found in average recoveries or between the independent method and the method under development.

A 28-day storage stability study was performed to determine long-term sample stability. Seventeen samples were collected for 4 h from an atmosphere containing 0.11 mg/m³ acrolein and 5 mg/m³ acetaldehyde and analyzed at 1-, 14- and 28-day intervals. The concentration of the atmosphere sampled was 0.11 ± 0.03 mg/m³, as determined by the independent method. The samples were stored at room temperature during the course of the study. Results with 95% confidence limits were 0.14 ± 0.02, 0.13 ± 0.02, 0.13 ± 0.01 mg/m³ for the three sets of analyses, respectively. There were no statistically significant differences in the mean concentrations, indicating that samples were stable for up to 28 days.

The relative standard deviations for the precision and accuracy and stability studies were found to be homogeneous using Bartlett's test (*9*) and pooled. This pooled sampling and analysis RSD for the method was adjusted for an assumed sampling pump error of 5% (9) and calculated to be 11.1% over the range of 0.13–1.50 mg/m³.

This method has been used in the NIOSH laboratories by three different analysts with no apparent intralaboratory variability. The method precisions of each analyst at each concentration level are reported in Table I. The analytical procedure is quite straightforward, using established analytical techniques. Samples collected using this method can be handled in a routine manner with no special precautions needed for shipment back to the laboratory for analysis.

Although this method in its present form does not appear to be suitable for monitoring acetaldehyde, it does show promise for the simultaneous determination of other low molecular weight aldehydes, such as formaldehyde. Research is currently under way in our laboratories to investigate the sampling and analysis of furfural and glutaraldehyde.

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Registry No. XAD-2, 9060-05-3; SP-2401-DB, 91466-38-5; Supelcoport, 91466-39-6; acrolein, 107-02-8; 2-(hydroxymethyl)-piperidine, 3433-37-2; 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane, 91443-94-6.

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