

Screening System for Phthalate Esters and Brominated Flame Retardants

Py-Screener Ver. 2



Are You Ready for RoHS Compliance?

Substances Restricted by RoHS II and Start Date

Restricted Substances	Max. Allowable Concentration	Date of Applicability				
		Cat 1 – 7	Cat 8 – 9	Cat 10	Cat 11	
Lead	0.1%	1 July 2006	22 July 2014	1 July 2006	22 July 2019	
Mercury	0.1%					
Cadmium	0.01%		22 July 2016 (In vitro diagnostic medical devices)			
Hexavalent chromium	0.1%		22 July 2017 (Industrial monitoring & control instruments)			
Brominated flame retardants	PBB		0.1%			
	PBDE	0.1%				
Phthalate esters	DEHP	22 July 2019	22 July 2021	22 July 2019	22 July 2019	
	BBP					0.1%
	DBP					0.1%
	DIBP					0.1%

The RoHS directive specifies the restricted use of 6 original substances, with an **additional 4 substances** added in, which take effect July 22, 2019. Businesses¹ operating with RoHS-regulated bodies that employ the use of these 10 hazardous substances in electronic and electrical components, for sale or redistribution, will be thus be affected.²

Unlike the first six restricted substances that can be easily measured by identifying specific elements, phthalate esters are organic molecules composed of only C,H, and O atoms.

This calls for a new chromatographic technique for the screening of these phthalate esters, which explicitly separates the four new restricted substances.

[1] Such businesses include businesses who sell to resellers, distributors or integrators that in turn sell products to RoHS-regulated counties.

[2] Such components include products, equipment, sub-assemblies, cables or spare parts

Applicable Products

 <ol style="list-style-type: none"> 1. Large Household Appliances 2. Small Household Appliances 3. IT and Telecommunications Equipment 4. Consumer Equipment 5. Lighting Equipment 6. Electrical and Electronic Tools 7. Toys, Leisure and Sports Equipment 	 <ol style="list-style-type: none"> 8. Medical Devices 9. Monitoring and Control Instrument
	 <ol style="list-style-type: none"> 11. Other EEE Not Covered by any of the Categories Above

RoHS II (Directive 2011/65/EU) not only expanded the scope of restricted substances, but also the products covered. Different compliance deadlines have been set for those newly added products. Electrical and electronic equipment (EEE) manufacturers are obliged to prepare for EU declaration of conformity and affix CE markings on finished products if the concentration of the substances in each homogeneous material is within the regulatory limits.

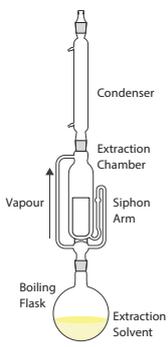
A Solution Designed to Fully Comply with the IEC method

IEC 62321-8

Determination of certain substances in electrotechnical products – Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS), gas chromatography-mass spectrometry using a pyrolyzer/thermal desorption accessory (Py/TD-GC-MS)

The Py/TD-GC-MS integrated assembly utilises gas chromatography-mass spectrometry coupled with a pyrolyzer/ thermal desorption unit.

- **Polymer samples may be directly inserted** into the desorption unit for the extraction of phthalates with a specified heating programme
- These thermally desorbed phthalates are then introduced into the GC and separated **by a capillary column before MS detection**
- They may be identified based on multiple parameters including retention times, m/z (quantitative and confirmation ions) and ion ratios
- Select Ion Monitoring (SIM) mode may also be used to **improve the limits of detection**
- A single-point calibration is applied for **screening and semi-quantitative analysis** of phthalates in the sample

GC-MS			Py/TD-GC-MS		
					
Conventional Soxhlet + GC-MS		Py-Screener			
					
~360 min Preparation	Use Organic Solvents	Accurate Determination	10 min Preparation	No Organic Solvents	Screening & Semi-Quantitation

Conventional Soxhlet extraction is typically required for determination of phthalates in GC-MS. While it enables accurate quantitation, it requires time-consuming pre-treatment protocols and uses large amounts of organic solvents.

In contrast, the Py/TD-GC-MS method does not require complicated pretreatment procedures and therefore can serve as an effective tool with faster processing of samples. For 90% of the time, screening suffices in deciding whether a sample has passed or failed the test.

Aside the analysis of phthalates, Py/TD-GC-MS can double up for screening of PBB and PBDE.

Making the Difficult Simple

The Py-Screener system is designed for easy operation, even for new users. Sample preparation toolkit, test standards, and a dedicated software for data processing are supplied with the system. User can also navigate through the self-help for maintenance support. By providing a complete solution, Shimadzu ensures that users of any level can perform phthalate screening with confidence.

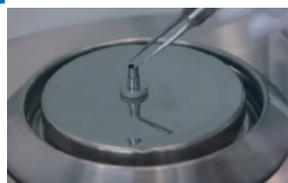
Easy to Operate Even for Novices

Prepare Samples without Organic Solvents*

Sample preparation is simple. Cut a small portion of test material, place it in a sample cup, and then weigh it. Watch the sample preparation videos when you need to be reminded on how to do it.



Preparation of a Phthalate Ester Standard



Weighing Using an Electronic Balance



Preparation of a Test Sample



Analytical Balances AP Series



Shimadzu balances product lineup

All Required Items Are Available

Specially Developed Test Standards and Toolkit

The solvent-less standards were specially developed with the market leader for RoHS testing (SGS, Japan). The certified standards can be used for sensitivity confirmation, quantitation, and blank tests. Cut a small piece consistently every time using a dedicated tool (micro puncher by Frontier Lab).

*Organic solvents are used only to clean tools and for retention time correction



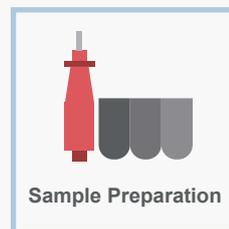
Standards Containing Phthalate Esters for Py-GC/MS



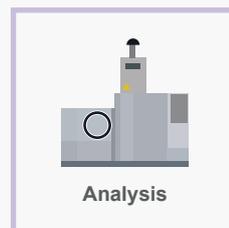
Sampling Toolkit

SHIMADZU

Py-Screener



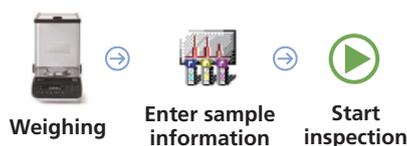
Sample Preparation



Analysis

User-friendly Operational Software

Batch template has been pre-created. Simply place your standards and samples orderly into the autosampler, key in the sample names and their weights, then start the automatic sequencing.



Options with Screening Methods

Shimadzu offers three default screening methods: (1) normal and (2) fast simultaneous screening of phthalate esters and brominated flame retardants; and (3) the even-faster screening of only the phthalate esters, which significantly reduces runtime.

	Vial#	Sample Name	Sample Amt.
1	1	Blank_Cup	0.5
2	2	Phthalate_STD_Blank	0.51
3	3	Phthalate_STD_100	0.51
4	4	Phthalate_STD_1000	0.51
5	5	ERM-EC691	0.51
6	6	Test_Sample	0.51
7	7	Test_Sample	0.51
8	8	Test_Sample	0.51

Easy to Operate Even for Novices
View All Results at a Glance

Information for all samples against all compounds are summarised in a single table. Compounds out of pre-set concentration ranges are coloured and flagged. This allows users to quickly pick up samples **to Review (orange)** and **the Outliers (red)**.



Report Confidently

The system is equipped with accuracy control functions. This ensures the reliability of blank concentrations, instrument sensitivity, and other data. Make use of the report templates to report your measurement results.



Data Processing



Maintenance

Py-Screener Software

The special software displayed on the monitor helps you navigate the required procedures. Even novices can operate the system using the software.

Ample Maintenance Support
Self-help for Maintenance Support

With the Maintenance Navigator, users can run through the procedures for the Pyrolyzer and GC-MS maintenance. Learn how to locate leaks and resolve them for long-term operation. Periodic Replacement Kits with regularly consumed parts are also provided to simplify maintenance and troubleshooting.



- ✓ Detailed maintenance steps with photos attached (Photos can be enlarged)
- ✓ A list of solutions for troubleshooting is included
- ✓ A list of consumables is included

Maintenance Navigator Windows

More Effective and Efficient Inspections with Four New Functions

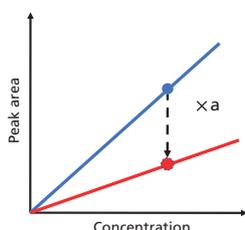
Py-Screener Ver. 2 retains the convenience of the previous Py-Screener, but is equipped with four new functions that enable even more effective and efficient inspections.

1. Simultaneous Inspections for Phthalate Esters and Brominated Flame Retardants (Total of 20 PBBs and PBDEs)

The system can perform batch inspections for phthalate esters and a total of twenty PBBs and PBDEs with between one and ten bromine atoms. With the new "correction factor database" function, the software automatically generates calibration curves for the compounds not included in the standard sample based on the calibration curve information of the standard sample, allowing the concentration of all of the above compounds to be calculated. A simultaneous screening method for phthalate esters, PBBs and PBDEs using Py-GC/MS has been studied for standardization under the international analytical standard IEC 62321 3-3.

Note: The same standard sample used in Ver. 1 is used in Ver. 2. However, calibration curve information obtained with conventional products cannot be used with Ver. 2.

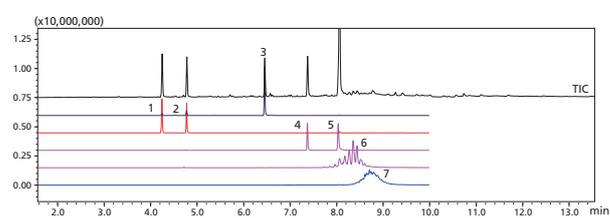
Expanding the number of target compounds using the new correction factor database function



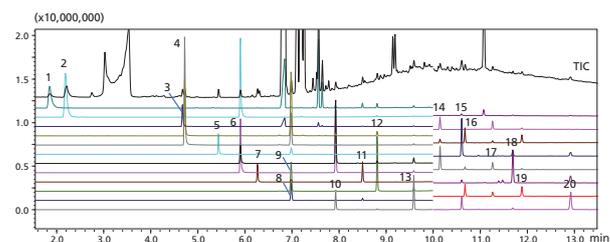
1. Calibration curve for compounds (substitute compounds) included in the standard samples
2. Multiply the calibration curve of the standard compounds by the sensitivity factor a
3. Calibration curve calculated for compounds not included in the standard samples

Equipped with the correction factor database function, which registers the area ratio information of the compounds (substitute compounds) included in the standard samples and the compounds not included in the standard samples.

A wide range of compounds can be quantified just with standards samples for some compounds.



Inspection results for seven phthalate esters (DIBP, DBP, BBP, DEHP, DNOP, DINP, and DIDP)



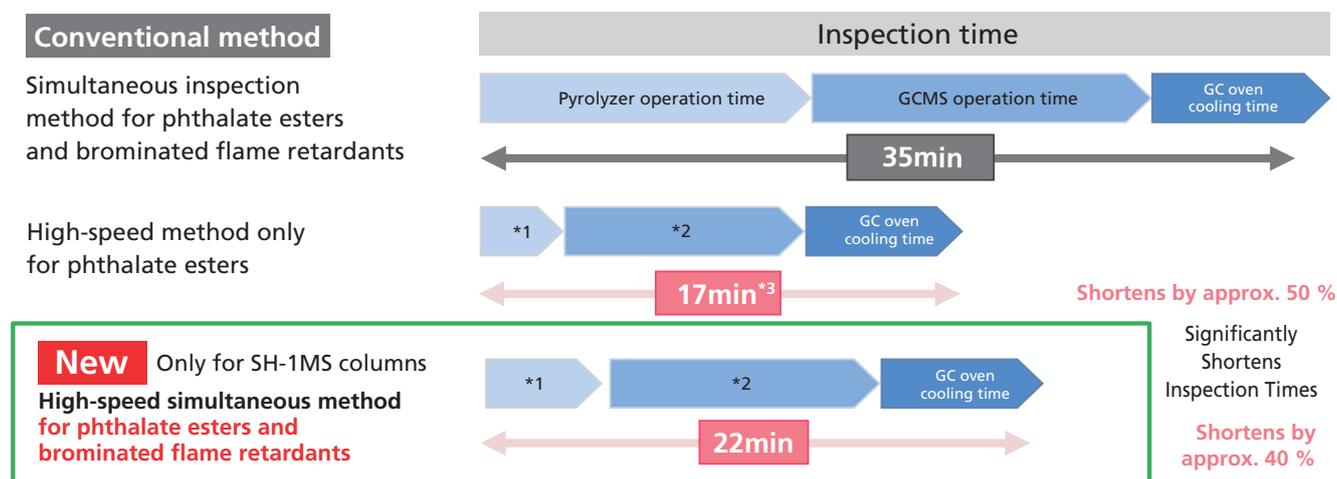
Inspection results for PBBs (total of ten with one to ten bromine atoms) and PBDEs (total of ten with one to ten bromine atoms)

2. Newly Developed High-Speed (22 Minute) Simultaneous Inspection Method for 7 Phthalate Esters and Brominated Flame Retardants

A method has been developed that significantly shortens simultaneous inspection times for phthalate esters and brominated flame retardants. This enables productive and reliable inspections for a wide range of regulated compounds.

Note 1: This edition also includes the conventional (35 minute) simultaneous inspection method for phthalate esters and brominated flame retardants, and an inspection method compatible with high-speed screening exclusively for phthalate esters.

Note 2: This simultaneous inspection method is only compatible with Shimadzu high-durability columns (SH-1MS with guard column).



*1 Pyrolyzer operation time *2 GCMS operation time *3 For UA-PBDE column. 19 min for SH-1MS column.

3. Phthalate Ester Screenings in Accordance with the European REACH Regulation

Since 2020, under the European REACH regulation, the same four phthalate esters (DIBP, DBP, BBP, and DEHP) regulated under the RoHS directive have become regulated in a wide range of molded items including toys and childcare articles.

Under the REACH regulation, regulatory concentration values are established with respect to individual concentration values and total calculated concentration values, which means that this regulation must be managed differently than the RoHS directive. This system is capable of automatic screening determinations with respect to the total calculated concentration of these four phthalate esters. It can also be used for phthalate ester inspections aimed at the REACH regulation.

Summary Results			
#	Name	<input checked="" type="checkbox"/> Sample R2	Conc.
<input checked="" type="checkbox"/>			
<input checked="" type="checkbox"/> 1	DIBP		141.83
<input checked="" type="checkbox"/> 2	DBP		372.04
<input checked="" type="checkbox"/> 3	BBP		302.52
<input checked="" type="checkbox"/> 4	DEHP		447.40
<input checked="" type="checkbox"/> 5	DNOP		----
⋮			
<input checked="" type="checkbox"/> 30	Total PBDEs		0.00
<input checked="" type="checkbox"/> 31	Total PBBs		0.00
<input checked="" type="checkbox"/> 32	DIBP, DBP, BBP, DEHP		1263.80

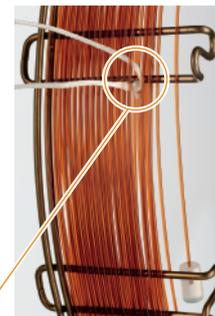
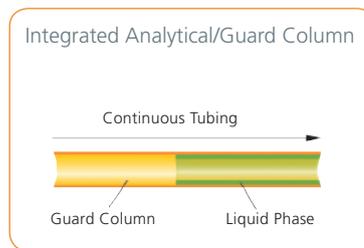
Individual concentrations of DIBP, DBP, BBP, and DEHP **Screening for RoHS**

Total concentration of DIBP, DBP, BBP, and DEHP **Screening for REACH**

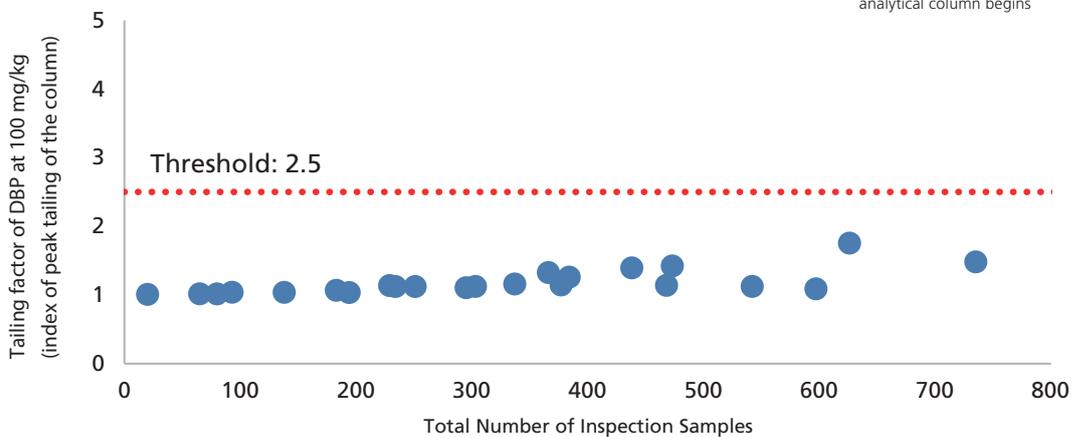
4. High Durability Columns Dedicated for Py-Screener Ver. 2

The system is now compatible with inspections with Shimadzu's SH-1MS high-durability column, which includes a guard column as part of its design. This reduces the maintenance burden and running costs by limiting column deterioration, even for customers who screen frequently.

The guard column is integrated, so there are no concerns about leaks due to the guard column connection or adsorption and decomposition of compounds targeted for screening at the connection site.



String indicates where the analytical column begins



Results of a durability test using the high-durability column (SH-1MS with integrated guard column) dedicated for Py-Screener Ver. 2

Maximize Your GCMS for RoHS (II) Analysis

Shimadzu GCMS is able to simultaneously accept installation of two narrow-bore capillary columns into the MS, thus allowing user to simply select the analysis mode and choose the associated injection port, without the need to physically modify the column installations.

We hereby present to you the only GCMS that accommodates both pyrolyzer and the liquid sample injector.

AOC-20i+s Plus
The autosampler for liquid injection of up to 150 sample vials

GCMS-QP2020 NX
The highly stable MS up to even m/z 1090



EGA/PY-3030D + AS-1020E
The pyrolyzer with autosampler for screening of up to 48 sample cups

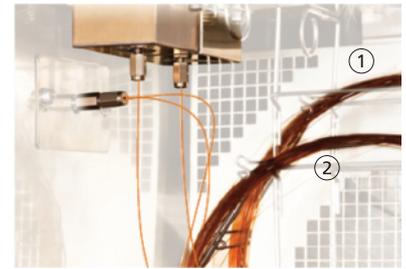
Nexis GC-2030
The high capacity GC that accommodates multiple columns for Twin Line MS

Techniques (As mentioned in IEC 62321-8)	Operating Principle			
	Sample Introduction	Distinguishing Phthalates	Compound Identifiers	Instrument Capability
Py/TD-GC-MS	Thermal Desorption using Pyrolyzer	Separation by a GC capillary column	<ul style="list-style-type: none"> Retention Time m/z (main and reference ions) Ion Ratio 	Screening
GC-MS	Soxhlet Extraction*	Separation by a GC capillary column	<ul style="list-style-type: none"> Retention Time m/z (main and reference ions) Ion Ratio 	Determination
IAMS (Found in informative annex)	Direct Introduction	No separation; All thermally desorbed sample molecules (M) form adducts (M + Li ⁺) with Li ⁺ in the reaction chamber	<ul style="list-style-type: none"> Single m/z (main ion) 	Screening
LC-MS (Found in informative annex)	Soxhlet Extraction	Separation by a HPLC column	<ul style="list-style-type: none"> Retention Time m/z (main and reference ions) Ion Ratio 	Determination

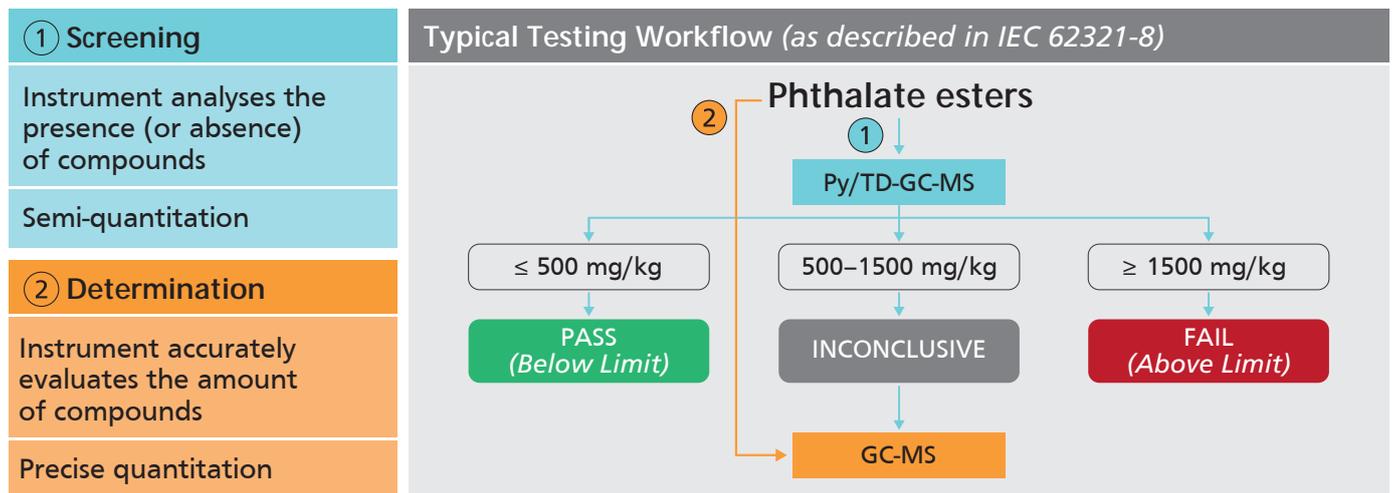
*For a THF-soluble polymer (e.g. PVC), alternative extraction procedure (extraction by dissolution in THF using sonication and precipitation of polymer matrix) may apply.

Twin Line eliminates the need to swap columns

Two column outlets can be inserted directly into the MS interface. Using a super large-capacity turbomolecular pump, Shimadzu GCMS maintains the sensitivity on each flow line that is equivalent to that when a single column is used. Therefore, columns suitable for both screening analysis (1) and precise quantitation (2) can be simultaneously installed to the MS.



*Twin Line does not support simultaneous analysis of the two lines



Applicable Phthalate Esters							Additional Compounds <small>(These compounds can be analysed using the same system, but are not target compounds of IEC 62321-8)</small>	Techniques
DIBP	DBP	BBP	DEHP	DNOP	DINP	DIDP		
●	●	●	●	●	●	●	e.g. Brominated Flame Retardants (PBB & PBDE)	Py/TD-GC-MS
●	●	●	●	●	●	●	e.g. Brominated Flame Retardants (PBB & PBDE)	GC-MS
X	X	●	X	X	●	●		IAMS
X	X	●	●	●	●	●	e.g. Hexabromocyclododecane (HBCDD)	LC-MS

● Screening ● Determination X Non-quantifiable due to interference



Screening



EDX-7200 / EDX-7000 /
EDX-LE Plus

- Hexavalent Chromium (Cr⁶⁺)
- Lead (Pb)
- Mercury (Hg)
- Cadmium (Cd)
- Poly-Brominated Flame Retardants (PBB/PBDE)



GCMS-QP2020 NX
with Py-Screener

- Phthalate Esters (DEHP/BBP/DBP/DIBP)
- Poly-Brominated Flame Retardants (PBB/PBDE)



Determination



UV-1280

- Hexavalent Chromium (Cr⁶⁺)



ICPE-9820

- Lead (Pb)
- Mercury (Hg)
- Cadmium (Cd)



GCMS-QP2020 NX
with AOC-20i+s Plus

- Phthalate Esters (DEHP/BBP/DBP/DIBP)
- Poly-Brominated Flame Retardants (PBB/PBDE)

Applicable Systems and Software for Py-Screener

GC-MS	: GCMS-QP2020 NX, GCMS-QP2020, GCMS-QP2010 Ultra
Pyrolyzer	: EGA/PY-3030D multi-shot pyrolyzer
Autosampler	: AS-1020E auto-shot sampler
GC/MS Workstation	: GCMSsolution (Ver. 4.53 or later) + LabSolutions Insight (Ver. 3.8 SP1 or later)
Py Workstation	: EGA/PY-3030D Control (Ver. 1.54 or later)

Caution

1. Note that there are no guarantees regarding the accuracy of the information contained in the method files, or the usefulness of the information obtained from the results of their use.
2. In order to accurately identify the registered substances, perform the measurements using the system conditions in the method files contained in the product.

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