

IDENTIFYING BLACK TONERS USING FTIR AND PYROLYSIS-GC/MS

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ABSTRACT: For the analysis of toner using Fourier transform infrared spectroscopy (FTIR) and pyrolysis gas chromatography with mass selective detection (pyrolysis-GC/MS) a previously reported sampling method using a heat transfer of the toner from the paper to a medium was revised to give more stable results whilst causing less damage to the document. To sample the toner home made stainless steel discs with polished surfaces are heated to 180°C and then applied to the document for about two seconds. The toner adhering to the discs gives a good representative sample and is used for both methods of analysis. No visible damage is done to the document.

The analysis of the toner consisted of two parts, a screening method using FTIR and a highly discriminative method applying pyrolysis-GC/MS. For the screening the FTIR microscope in transmission mode was found to give the best results, dividing the toner test set into several different classes. Further differentiation within the toner classes was achieved with pyrolysis-GC/MS.

KEY WORDS: Questioned documents; Toner; Photocopy; Fourier transform infrared spectroscopy; Pyrolysis-GC/MS; Heat transfer sampling.

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INTRODUCTION

In the past many different physical and chemical methods have been used to determine whether two documents were produced by the same photocopier, fax machine or electrophotographic printer. The physical methods vary from the comparison of toner morphology [5, 12], trash marks [13], indentations from grip and roller mechanisms [12] and white divots to the decoding of ID-tracing codes on colour photocopies. Depending on the amount and quality of the trace evidence found on the documents, these physical methods can have an extremely high evidential value often leading to conclusions bordering on certainty that two documents were produced on one and the same machine. Conclusions that two documents were not produced on the same machine can often only be drawn on the basis of physical evidence if the documents in question can be placed within a known time frame

from which sufficient non-questioned material is available that has been produced on the same machine. Chemical methods reported in the past have been used for the comparison of: the organic content (polymers) via FTIR [1, 3, 6, 7, 9, 10, 11, 12, 14, 15] and pyrolysis-GC/MS [2, 3, 4, 7, 8, 12, 15], the dye content by thin layer chromatography and the elemental content by energy dispersive X-ray microanalysis [3]. Recently also ICP/MS has come into the picture as a promising method in this area. The conclusions drawn from chemical analysis are often weaker than those drawn from physical examinations, where the strength of the conclusions is often directly related to the method of analysis and the size of the database of analysed samples that is accessible. The accessibility of these databases is often the main problem for most laboratories, as setting up and maintaining such a database is an enormous task. The conclusions drawn from chemical analysis are therefore often limited to exclusions (two documents were not produced on the same machine). In the positive sense non-exclusions or relations to the same brand or type of machinery (it cannot be excluded that the documents were made on the same machine or different machines of the same make and model or from the same manufacturer).

Besides the instrumental methods of analysis quite a bit of research has also been put into the different sampling methods to remove the toner from the paper. Methods reported until now are in situ analysis on the paper [3], scraping or slicing a toner sample from the paper [6, 7, 9, 10, 11], extraction of the toner using various solvents [7, 9, 10, 11] and heat transferring the toner from the paper onto another substrate [1, 3, 4, 11]. This paper provides the document examiner with a revised method of heat transfer sampling. Techniques applying heat transfer sampling reported until now have used a soldering iron as a heat source. This was done by either pressing the iron (equipped with a special tip) to the reverse side of the document whilst a sampling device (glass, metal foil, stub, etc.) was in contact with the toner on the front side of the document or by pressing the iron directly against the sampling device held against the toner on the document. Experimenting with these methods we have found that the soldering iron applied directly to the document often leaves burn marks and that these methods are not very reliable and easy to use. The revised method described in this paper using stainless steel discs has overcome these problems and is reliable, fast and easy to use.

EXPERIMENTAL/METHOD

Materials

The test set of black toners consisted of prints or copies from a: Hewlett Packard 4000, laser printer; Rex Rotary 2825, photocopier; Lexmark Optra E plus, laser printer; Agfa X210, photocopier; Panasonic FP 7728, photocopier; Xerox 5614, photocopier; Xerox 5815, photocopier; Brother HL 760, laser printer; Hewlett Packard 6L, laser printer; Brother HL 1660, laser printer.

Sampling devise

Sampling discs consisted of 2 mm thick stainless steel discs with a diameter of 10 mm. One side of the discs had been polished.

Instruments

Sampling

The sampling discs were heated to 180°C on an IKA-RET thermostat with a built in temperature display.

FTIR

FTIR-microscopic transmittance/absorbance analyses were performed on a Bruker IFS 45 spectrometer with a Mercury-Cadmium-Telluride detector. The samples were placed on a single-crystal KBr disc.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analyses were performed on a Bruker IFS 45 spectrometer with a Mercury-Cadmium-Telluride detector and a Spectra Tech DRIFTS unit.

FTIR-microscopic reflection-absorption analyses were performed on a Biorad UMA 150 spectrometer with a microscope and a Mercury-Cadmium-Telluride detector. Spectra were measured directly from the sampling disc.

All FTIR spectra were compiled of 256 scans with a resolution of 4 cm⁻¹ in the range of 4000–650 cm⁻¹.

Pyrolysis

Pyrolysis was performed using a CDS Pyroprobe 1000 with a platinum ribbon on which the toner was deposited. The pyrolysis programme was as follows:

- drying at 80°C for 1 s;
- ramp of 500°C per ms;

- pyrolysis at 700°C for 10 s;
 - cleaning at 1200°C for 10 s.
- The interface temperature was set at 260°C.

GC

The gas chromatograph used was a Finnigan Mat GCQ with a mass selective detector. A Chrompack WCOT fused Silica column, 50 m × 0.25 mm, with a CP-SIL coating was used with a Helium flow of 35 cm/min and a split ratio of 1:10. The temperature programme was as follows:

- initial temperature was 40°C;
 - hold initial temperature for 3 min;
 - ramp 10°C/min;
 - final temperature 250°C;
 - hold final temperature for 10 min.
- The analysis time was 34 min.

MS

The mass spectrometer used was a Finnigan MAT Automass II, which is a quadrupole instrument. The scan range was from 35–400 amu with one scan per 500 ms.

Procedure

Sampling

The sampling discs were placed, polished side down, on the hot thermostat (180°C) for a few minutes before sampling. With a pair of tweezers a disc was lifted from the thermostat and swiftly transferred to the surface of the document containing the toner to be sampled. The disc was pressed, polished side down, against the toner during 1–2 seconds and then lifted off the paper again with the tweezers. After cooling the disc was checked under a microscope to see if sufficient toner had adhered to the surface, see Figure 1. The discs may then be labelled and stored away awaiting analysis of the toner. After use the discs were cleaned with a tissue and acetone followed by a visual check for residue under a stereomicroscope.

FTIR analysis

For microscopic transmittance/absorbance measurements samples were scraped from the sampling disc and placed onto a single-crystal KBr disc.

Measurements performed with the DRIFTS unit were not true diffuse reflectance measurements but more or less a combination of diffuse reflectance and reflection-absorption. To perform these measurements the

Fig. 1. A metal sampling disk before and after heat transfer sampling of the toner.

toner was transferred to the metal alignment disc of the DRIFTS unit. This disc was then placed in the unit and a measurement was made.

Microscopic reflection-absorption measurements were made by positioning the sampling disc with the toner under the FTIR microscope set to reflectance.

Pyrolysis-GC/MS analysis

A very small amount of toner (2–10 µg) is scraped off the sampling disc and transferred to the pyroprobe ribbon. The toner is fixated onto the ribbon during the drying cycle at 80°C for 1 s. The probe is placed into the interface that is then flushed with Helium for 5 min to eliminate the presence of oxygen. After synchronisation with the gas chromatograph the pyrolysis programme is run. Each analysis is followed by a blank run without toner sample.

RESULTS AND DISCUSSION

Sampling methods

Different sampling methods were examined of which the advantages and disadvantages are listed in Table I.

TABLE I. EXAMINATION OF THE DIFFERENT SAMPLING METHODS

| Sampling method | Advantage | Disadvantage |
|-------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| In situ measurement on the document. | Fast. | Destructive, sample chamber limits the size of the paper; Interference from the paper. |
| Scraping/slicing of toner from the document. | Fast. | Difficult to sample without paper residue. |
| Dissolving the toner. | Clean samples. | Destructive; Possible contamination from the paper; Use of solvents. |
| Heat transfer with a soldering iron pressed against the rear of the document onto KBr disc: – onto aluminium foil; – onto a sampling disc. | Clean samples. | The up side down positioning of the sample area onto the transfer medium; Burn marks caused by soldering iron due to excessive heat. Timing is difficult; Coating on aluminium foil interferes with spectrum. |
| Heat transfer with a soldering iron pressed against transfer medium on the front of the document: – onto a sampling disc; – onto a glass slide. | Clean samples; Simple to use; No directly visible destruction of document. | Timing is difficult, medium takes time to heat up; Temperature difficult to control. |
| Heat transfer to a sample disc clamping and heating in a stove at 200oC for 15 min. | Clean samples. | Destructive (heating of document); time consuming. |
| Heat transfer to a preheated sampling disc. | Clean samples; Simple to use; Fast; Reliable; Easy storage of samples; No directly visible destruction of document. | Swift action is necessary to remove the disk from the document before the toner re-solidifies. |

From this table it can be seen that the proposed heat transfer technique using a metal sampling disc combined a number of advantages such as ease of use, reliability, no interference from the paper, limited damage to the document and easy storage of the samples. Other examined methods all have one or several disadvantages ranging from the destruction of part of the document to the efficiency of the method.

FTIR

Of the different FTIR measuring techniques examined for this paper the spectra obtained with the FTIR microscope in the transmittance/absorbance mode, see Figure 2, are the best defined and most reproducible.

The spectra obtained with the DRIFTS unit, see Figure 3, are also quite well defined, however the reproducibility is less due to problems with the exact positioning of the alignment disc. Also the disturbance from water vapour is larger due to the larger compartment size, making it more difficult to eliminate water vapour.

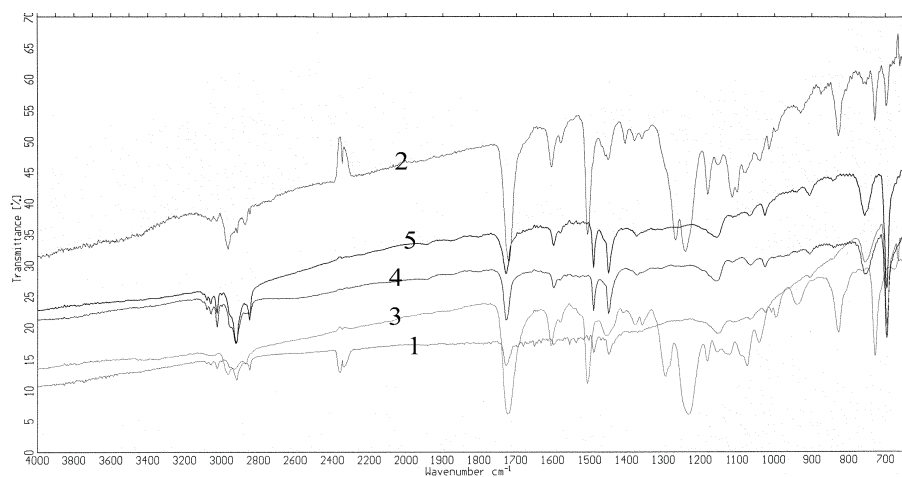


Fig. 2. FTIR microscopic transmittance spectrum of toners 1–5.

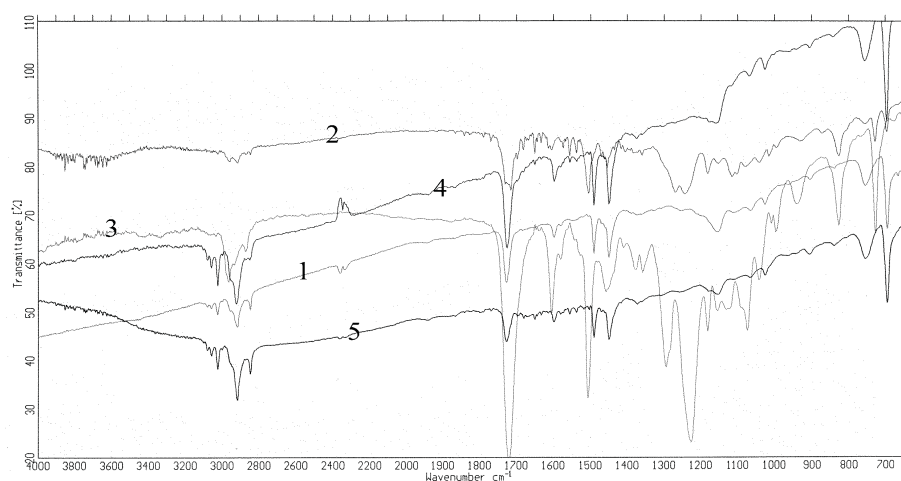


Fig. 3. FTIR spectrum of toners 1–5 with measured DRIFTS unit.

The reflection-absorption spectra were unsuitable for comparison due to a sinusoid disturbance of the baseline caused by internal reflections within the thin polymer film, see Figure 4.

With FTIR it was possible to divide the ten toner samples of our test set into three different classes. Table II shows the separation of the samples into these classes along with some of the characteristic bands belonging to each class.

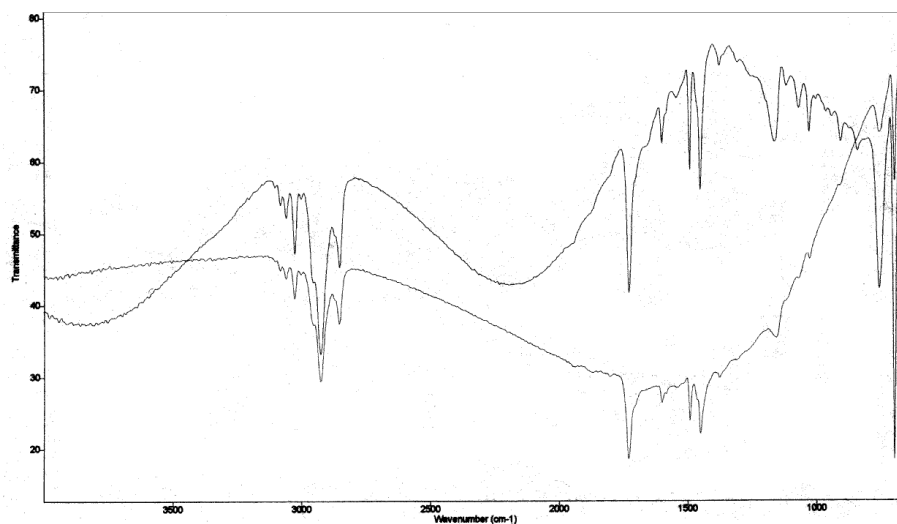


Fig. 4. Microscopic reflection-absorption FTIR spectra of two toners.

TABLE II. INTERPRETATION OF THE FTIR SPECTRA OF THE TONERS IN THE TEST SET

| Class | Toner samples | Characteristic features |
|-------|-------------------------|------------------------------------------------------------|
| I | 2 and 9 | 1250 cm^{-1} and 1280 cm^{-1} |
| II | 1, 4, 5, 6, 7, 8 and 10 | Absence of 1250 cm^{-1} and 1280 cm^{-1} |
| III | 3 | 1265 cm^{-1} and 1100 cm^{-1} |

Pyrolysis-GC/MS

Pyrolysis-GC/MS was found to be a highly discriminating technique for the analysis of toners. Using the method described earlier good spectra were acquired with a good reproducibility in retention time of the different components (Relative standard deviation 0.12%). Using the underlying mass spectra, see Figure 5, many of the different components of the chromatograms could be identified.

A list of components in the different samples is given in Table III. Not all components could be identified from their mass spectra, this is however not a necessity for comparison purposes.

In comparing the chromatograms of the toner test set we were able to identify 7 classes on the basis of the presence or absence of certain components. The remaining toners could be further distinguished on the basis of peak ratios. Due to the limited reproducibility of peak heights and ratios when using pyrolysis only large differences in ratios were used, see for an ex-

ample Figure 6. An overview of the total differentiation process is given in Figure 7.

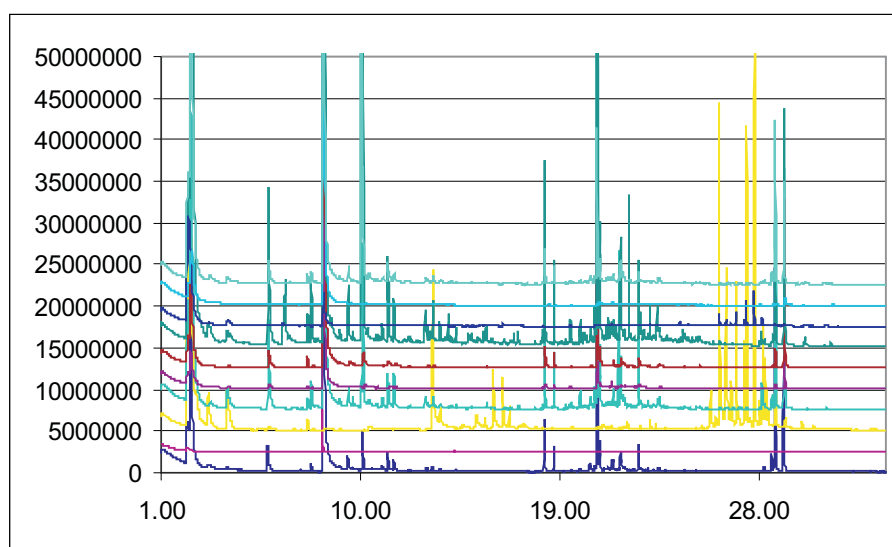


Fig. 5. Results from pyrolysis-GC/MS analysis of the toner set.

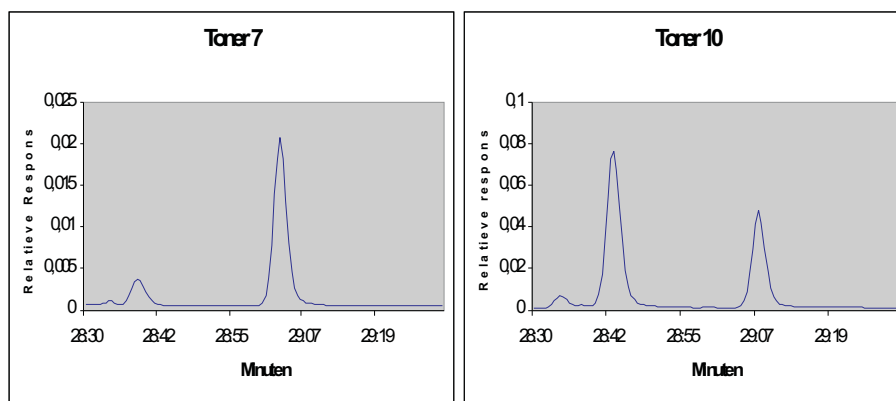


Fig. 6. Differences in relative intensities of two peaks used for differentiation.

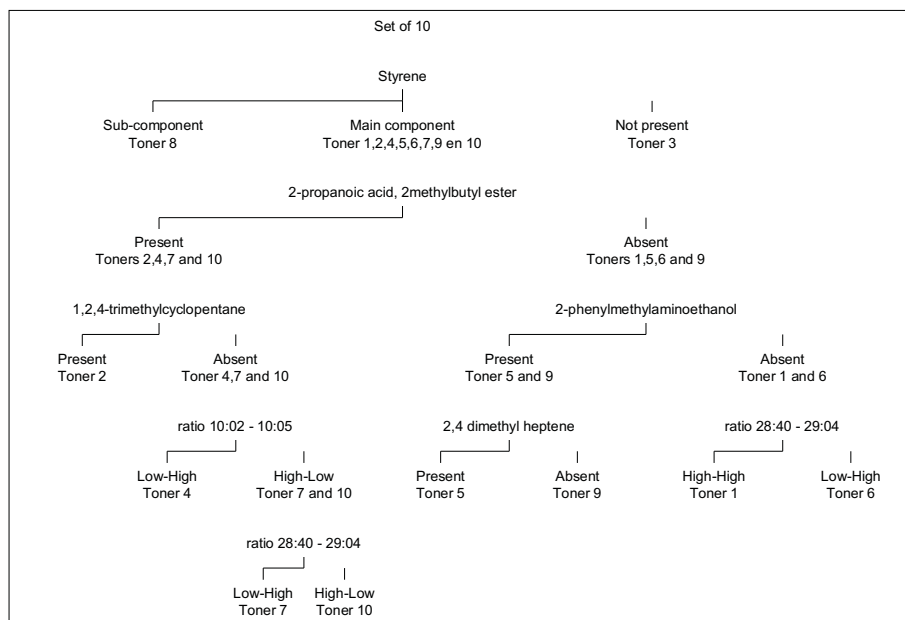


Fig. 7. Pyrolysis-GC/MS differentiation process.

CONCLUSION

An analysis scheme for the chemical comparison of toners using FTIR and Pyrolysis-GC/MS has been considered together with a revised heat transfer sampling method to sample the toner from the paper in an almost non-destructive manner. This revised sampling technique using preheated stainless steel discs to sample the toner on the paper was found to be extremely reliable and easy to use, leaving no visible trace on the document.

It was found that of the FTIR methods examined the FTIR-microscope in the transmittance/absorbance mode, applying a small sample of toner onto a KBr crystal was the most reliable method of analysis, giving good representative spectra with a reasonably flat baseline free of interference. This FTIR method was found to be suitable as an efficient screening method for toners dividing the test set into a reasonable number of classes. This method is however not suitable for drawing conclusions on common origin of toner samples as the method lacks sufficient discrimination power. If no differentiation between toner samples is made using FTIR then pyrolysis-GC/MS may be used. This method is far more discriminative than FTIR but also more labour intensive.

TABLE III. IDENTIFICATION OF THE DIFFERENT COMPONENTS FROM THE TONER SAMPLES AFTER PYROLYSIS-GC/MS

[illegible]

| Component | Rt | Toner 1 | Toner 2 | Toner 3 | Toner 4 | Toner 5 | Toner 6 | Toner 7 | Toner 8 | Toner 9 | Toner 10 |
|------------------------------------------------|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|----------|
| ??? | 10:30 | x | | | | | | | | | |
| ??? | 10:42 | x | | | | | | x | | x | x |
| 1-methyene-2-propenylbenzene | 10:58 | x | | | x | | | | | | x |
| Indene | 11:12 | x | | | x | x | x | x | | | x |
| 3 butenyl benzene | 11:14 | x | x | | x | x | x | x | | x | x |
| 1-methylene-propyl benzene | 11:29 | x | x | | x | x | x | x | | x | x |
| 1,1'-[1,2-dimethyl-1,2-ethanediyl] bis-benzene | 12:11 | x | x | | | | | x | | | |
| 3-tertradecene | 12:16 | x | | | | x | | | | | |
| 1-propamine, n phenylmethylene | 12:57 | x | | | | x | x | x | | | x |
| 1-methyl-2-cyclopropen-1-yl | 13:01 | x | | | | x | x | x | | | x |
| 1 methyl-1h-indene | 13:05 | | | | | | | x | | | |
| X methylene-Y-propenyl benzene | 13:12 | x | | | | | | | | x | x |
| 1,1a,6,6a-teretrahydro cyclopropa[a]indene | 13:15 | x | x | x | | x | x | x | | x | x |
| Naftalene | 13:35 | x | | x | | x | | x | | | |
| 3-methyl-hexanol | 13:52 | x | | | | x | | | | | |
| 1,2 dihydro-2-methyl naftalene | 14:00 | | | | | | | x | | | |
| ??? | 14:07 | | | | | | | | | | x |
| 2-propenoic acid 6-methylheptyl ester | 14:15 | | x | | | | | | x | | |
| 1-cyclohexe-1-yl benzene | 14:17 | x | | | x | | | x | | | |
| ??? | 14:20 | | | | | | | | | | x |
| Naftalene iets | 14:52 | | | | | | | x | | | |
| 1,2-dihydro-6-methyl naftalene | 15:00 | x | | | | | | x | | | x |
| ??? | 15:22 | x | | | | x | | x | | | x |
| 1-methyl naftalene | 15:32 | x | | | | | | x | | | x |
| Nitric acid, nonyl ester | 15:41 | | | | x | x | x | x | | | x |
| ??? | 15:54 | x | | | | | | x | | | x |
| ??? | 15:58 | x | | | | | | | | | |
| Thieno(2,3-e) benzofuran | 16:02 | x | | x | | | | | | | |
| ??? | 16:06 | x | | | x | | | | x | | |
| ??? | 16:29 | x | x | x | | | | | x | | |
| Trichloroeicosylsilane | 16:46 | x | x | x | | x | | | x | | |
| ??? | 16:55 | x | | | | x | | x | x | | |
| Diphenylmethane | 17:07 | x | | | x | | | x | | | x |
| 1,1'ethylidene bisbenzene | 17:52 | x | | | x | | | | | | x |
| ??? | 18:05 | x | x | | | x | | | | x | |

| Component | Rt | Toner 1 | Toner 2 | Toner 3 | Toner 4 | Toner 5 | Toner 6 | Toner 7 | Toner 8 | Toner 9 | Toner 10 |
|----------------------------------------------------------|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-------------|
| 3-eicosene | 18:11 | x | x | x | | x | | x | | | x |
| Bibenzyl | 18:17 | x | x | | x | x | x | x | | x | x |
| ??? | 18:38 | x | | | | | | | | | |
| 1,1'(1-methyl-1,2-ethaned iyl)bis-benzene | 18:42 | x | x | | x | x | x | x | | x | x |
| ??? | 18:57 | | x | | | | | | | | |
| a-Methyl stilbene | 19:16 | x | | | | | | | | | |
| ??? | 19:20 | | | | | x | x | | | | |
| ??? | 19:23 | | | | | | x | | | | |
| 2,6,10,14 tetramethyl- heptadecane | 19:27 | x | x | x | | x | x | | x | | x |
| ??? | 19:30 | x | | | | x | | x | | x | x |
| ??? | 19:36 | x | | | | x | | | | x | x |
| ??? | 19:43 | x | | | | | | | | x | x |
| ??? | 19:51 | x | | | | | | | | | x |
| 1,1'-[1,3-propanediyl]bis- benzene | 19:54 | x | | | x | x | | x | | | x |
| ??? | 20:05 | x | | | | | | | | | |
| ??? | 20:08 | x | | | | | | | | | |
| ??? | 20:12 | x | | | | x | | | | | |
| Benzoic alcohol | 20:21 | | | | | | | | | | x |
| Diphenylethylene | 20:24 | | | | | x | | | | | x |
| ??? | 20:37 | x | x | | x | | | x | x | | x |
| ??? | 20:40 | x | x | | x | x | x | | | x | x |
| 2,6,10,14 tertramethyl hexadecane | 20:45 | | | | | | | | x | | |
| ??? | 20:48 | x | x | | x | x | x | x | x | x | x |
| ??? | 20:52 | x | | | | | | | | x | |
| ??? | 21:19 | | x | x | | x | x | x | x | x | x |
| ??? | 21:23 | | | | | x | | | | | |
| 3 octadecene | 21:39 | | | | x | | | | | | |
| 1,1'-[1-cyclobutene-1,2-diy l]bis-benzene | 21:43 | x | | | x | x | x | x | | x | x |
| ??? | 21:46 | x | | | | | | x | | x | x |
| ??? | 21:54 | | | | | | | x | | | |
| ??? | 22:01 | | x | | | | | | | | |
| ??? | 22:33 | x | x | | x | x | x | x | | x | x |
| ??? | 23:07 | | x | | | | | | | | |
| 2-phenylnaftalene | 23:24 | | | | | | | | | | x |
| 3-benzyl-1,2dihydronaftal ene | 23:29 | | | | | | | | | | x |
| ??? | 24:23 | | x | | | | | x | x | | |
| 1,1',1'',1'''-1,2 ethanediylindenetetra bisbenzene | 24:38 | | | | | | x | | | | |

| Component | Rt | Toner 1 | Toner 2 | Toner 3 | Toner 4 | Toner 5 | Toner 6 | Toner 7 | Toner 8 | Toner 9 | Toner 10 |
|------------------------------------------------|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-------------|
| ??? | 24:44 | | x | | | | | | x | | |
| Beta methyl beta phenyl, benzeneethanol | 25:11 | | | | | | x | | x | | |
| ??? | 25:20 | | | | | | | | | | |
| ??? | 25:46 | | x | x | | | | | x | | |
| ??? | 26:08 | x | x | x | | | | | x | | |
| ??? | 26:27 | x | x | x | | | | | x | | |
| Benzenemethamine, n- hydroxy-n-phenylmethyl | 26:44 | | | | | | x | | | | |
| ??? | 26:55 | x | x | x | | | | | x | | |
| ??? | 27:15 | x | x | x | | | x | | x | | |
| ??? | 27:22 | x | x | x | | | | | x | | |
| ??? | 27:43 | x | x | x | | | | | x | | |
| ??? | 27:57 | | x | | | | | | | | |
| ??? | 28:01 | | | | | | x | x | | | x |
| ??? | 28:05 | | x | | | | | x | x | | x |
| ??? | 28:11 | | | | | | | | x | | x |
| ??? | 28:14 | | x | | | | x | | | | x |
| ??? | 28:21 | | | | | | x | | | | |
| ??? | 28:33 | | | | | x | | | | x | |
| ??? | 28:40 | x | x | x | x | x | x | x | x | x | x |
| ??? | 29:06 | x | x | x | x | x | x | x | x | x | x |

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