

Superconductivity Centennial Conference

# Identification of liquids by high- $T_c$ Josephson THz detectors

Y. Divin<sup>a</sup>, M. Lyatti<sup>a,c</sup>, U. Poppe<sup>a</sup>, K. Urban<sup>a,b</sup>,

<sup>a</sup>*Peter Grünberg Institute (PGI-5), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

<sup>b</sup>*Ernst Ruska-Centre, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

<sup>c</sup>*Kotelnikov Institute of Radio Engineering and Electronics of RAS, 125009 Moscow, Russia*

## Abstract

Fast and reliable detection of liquids will be required for future checkpoint screening techniques. Recently, a new electromagnetic-wave concept based on our high- $T_c$  Josephson detectors and Hilbert spectroscopy has been suggested to distinguish between liquids. This technology covers a spectral range of main dispersions of liquids, from a few GHz to a few THz, and thus significantly enhances reliability of identification. The high- $T_c$  detectors, due to a power dynamic range of more than five orders, might guarantee short identification times. Several demonstration set-ups of liquid identifiers, consisting of high- $T_c$  Josephson detectors, integrated in Stirling coolers, and polychromatic radiation sources, have been developed and characterized. Reflection polychromatic spectra of various liquids in plastic containers have been measured at the spectral range of 15-500 GHz with total scanning time down to 0.2 second. Reliable identification of liquids, both benign and threat, within an accuracy of 0.3% was demonstrated using water as a reflectance reference. The reflectance values for 30% $H_2O_2/H_2O$  solution at frequencies of 30 and 100 GHz were practically undistinguishable from that of for pure water, but an increase of the relative reflectance from 1.017 at 282 GHz to 1.033 at 434 GHz has been found. Last circumstance will be used for optimization of the identifiers.

© 2012 Published by Elsevier B.V. Selection and/or peer-review under responsibility of the Guest Editors.  
Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

*Keywords:* High-temperature superconductors; Hilbert transform spectroscopy; Josephson radiation detectors; liquids; security .

## 1. Introduction

Bottled liquids which might contain flammables, explosives or their components are a severe security concern. Safety inspections of hand luggage at airports, seaports, rail stations or other public places must be very reliable, fast and very specific to the liquids in order to avoid false alarms. For the identification of the content, the bottles should be unopened with no traces outside the bottle. Also, liquids which can act as precursors for explosives like hydrogen peroxide ( $H_2O_2$ ) and acetone have to be identified. There exist a lot of such dangerous substances in the form of pure liquids, liquid mixtures, and emulsions [1].

Among various detection methods, techniques which use electromagnetic radiation in the gigahertz and terahertz range are considered to be very promising [2]. Measuring the dielectric permittivity of the

liquid under concern over a large frequency range which contains the main dispersion region of most liquids and comparing it with a reference databank is an appropriate method as it can provide a unique fingerprint of the bottle content. A spectroscopic technique suggested by us is the Hilbert spectroscopy [3] in combination with high- $T_c$  superconductor Josephson detectors [4]-[7]. This technique can cover an extremely wide frequency range from a few gigahertz to a few terahertz. In comparison with conventional approaches, where only low frequency measurements are used, this method is much more reliable as one can cover the whole frequency range, where many different liquids of concern show a substantial change in dispersion and, therefore, in reflectivity. Especially in the case of mixtures of different liquids, a restriction to the low-frequency range will result in more false alarms as one can produce a wide range of permittivity values by changing the relative content of the mixture components.

Furthermore, the high- $T_c$  Josephson detectors allow a fast operation due to their high power dynamic range and high sensitivity. Here, we present a special setup of a Hilbert spectrometer placed on a Stirling cooler which allows broadband reflectance measurements of liquids. We show that an identification of liquids of concern including  $H_2O_2$  and acetone is possible by this technique as one can achieve an accuracy of around 0.3% even for short scanning times of a few seconds.

## 2. Experimental results

### 2.1. High- $T_c$ Josephson junctions

Reflection spectra were recalculated using available data for various liquids [6], and typical examples for some pure liquids are presented in Fig. 1. The main spectral range of dispersion for these liquids is rather broad and extends from around 1 GHz to around 1 THz. The differences in reflectance values for those pure liquids except for water and hydrogen peroxide are relatively high. This difference in reflectivity might be of different sign and show even lower absolute values for  $H_2O_2/H_2O$  mixtures depending on the concentrations [8].

For the liquid identifier presented here, it was sufficient to use  $YBa_2Cu_3O_{7-x}$  [001]-tilt bicrystal grain-boundary Josephson junctions with  $I_c R_n$ -values of 100-250  $\mu V$  (with critical current  $I_c$  and normal state resistance  $R_n$  of the junction), corresponding to characteristic frequencies of about 50 to 125 GHz, as most liquids show their main dispersion changes below around 1 THz. Junctions on MgO bicrystals were integrated with a broadband log-periodic antenna. [100]-tilt Josephson junctions on  $NdGaO_3$  with  $I_c R_n$ -values up to 8 mV at low temperatures would extend the upper frequency limit but only allow broadband detection at low frequencies instead of frequency selective detection [7].

The substrate with the Josephson junction and antenna was mounted on a cold finger of a cryocooler. For more than 10 years we have gained a lot of experience [9], [10] for the integration of high- $T_c$  Josephson detectors and Hilbert spectrometers into Stirling coolers of different types (SL200, AIM Infrarot Module GmbH and LSF9589, Thales Cryogenics B.V.). Special care with respect to magnetic shielding, temperature stability of the junction together with a cooled preamplifier and the broadband quasioptical coupling of the electromagnetic high frequency radiation to the junction was taken.

Our high- $T_c$  Josephson detectors demonstrate a power dynamic range of 50-60 dB for a detection bandwidth of 1 Hz [7]. With the noise level of 0.17  $nV/Hz^{1/2}$  of the cryogenic amplifier and a 1 ms time constant of the lock-in amplifier, we might achieve a value of 32 dB for the power dynamic range in our experiments leading to a signal-noise ratio sufficient to distinguish even the very small differences in the reflectivity's of  $H_2O$  and a 30% $H_2O_2/H_2O$  solution. For low frequencies (30-282GHz), we used a Josephson junction of  $R_n \approx 0.2 \Omega$ ,  $\delta f \approx 0.8$  GHz and  $I_c R_n \approx 100 \mu V$  at  $T=80$  K, whereas for high frequencies (250-470 GHz) we used a junction of  $R_n \approx 0.25 \Omega$ ,  $\delta f \approx 1.7$  GHz and  $I_c R_n \approx 500 \mu V$  at  $T=65$  K.

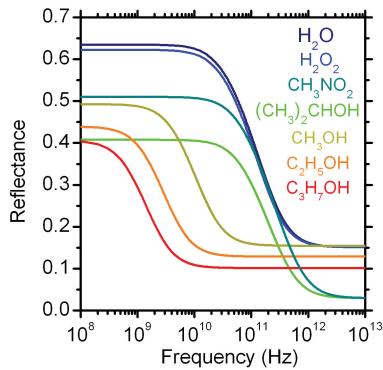


Fig. 1. Reflection spectra for several benign and threat liquids [6].

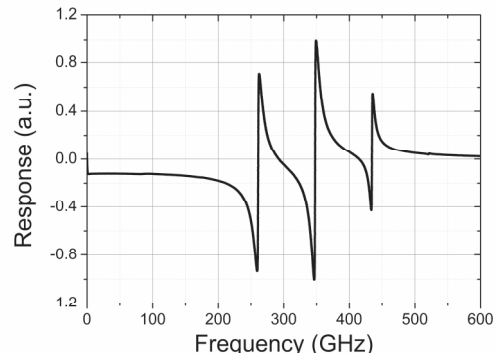


Fig. 2. Response  $\Delta I(V)$  to polychromatic radiation consisting of three lines at 261 GHz, 348 GHz and 435 GHz reflected from water.

## 2.2. Hilbert transform spectrometer

### 2.2.1. Principle of Hilbert spectroscopy

Hilbert spectroscopy was developed in the early 80<sup>th</sup> [3] and is based on the ac Josephson effect which establishes proportionality between the frequency  $f_j$  of an internal current oscillation in the junction and the voltage  $V$  applied across this device ( $f_j = 2eV/h$ ). When the Josephson junction is irradiated by monochromatic electromagnetic radiation, the Josephson oscillation frequency, due to internal nonlinear dynamics, is pulled to the frequency of the external radiation. Due to this frequency pulling, the current-voltage characteristic of the Josephson junction is modified around the voltage corresponding to the frequency of the external radiation. The current response  $\Delta I(V)$  of the junction, which is difference between the current-voltage characteristic with and without external radiation, is additive if more frequencies than a single frequency is irradiated on the junction. An example of such current response from a polychromatic radiation source consisting of three frequencies (261 GHz, 348 GHz and 435 GHz) is shown in Fig. 2. If an arbitrary continuous spectrum  $S(f)$ , covering a wide frequency range, is received by the broadband antenna on the junction one can recover it by a Hilbert transformation from the current response  $\Delta I(V)$ , the static  $I-V$  curve without external radiation and other measurable parameters like  $I_c$  and  $R_n$ . This is the basis for the Hilbert transform spectroscopy technique [3]. The technique can be applied if the Josephson junction can be very good described by the RSJ model, which is the case for our high- $T_c$  Josephson junctions. If the response of a single frequency, similar to one of the three resonance lines in Fig. 2., is transformed to the spectrum, one receives the spectral resolution of the spectrometer, which was between 0.8 and 1.7 GHz for our measurements depending on the junction temperature and the differential resistance at the voltage (or correspondingly frequency) of interest. The difference between the positions of the maximum and the minimum of the resonance in the current response, as e.g. seen in Fig. 2 gives an estimate for the spectral resolution.

### 2.2.2. Spectrometer setup for reflection measurements of liquids

The developed liquid identifier is consisting of several parts: several polychromatic radiation sources, a quasioptical pathway, where the radiation is focused to the liquid under concern in a special polyethylene (PE) container, and finally focused to the high- $T_c$  Josephson detector. There, the external radiation is analyzed after being reflected and modified in its spectral content by e.g. the dangerous liquid. In Fig 3. some details of the setup can be recognized. On the right side, we see the horn antennas from a low (1) and a high (2) frequency synthesized radiation source based on multiharmonic multipliers from

RPG GmbH [11]. The two sources are combined by a Cu-grid on a polyethylene (PE) foil (3) with a hole size of  $100\mu\text{m}$  transparent for high frequencies and being reflective for the low frequency part of the radiation. The elliptical mirror (4) focuses the radiation to the PE test cell (5) with a cylindrical (60mm diameter) outer surface, to a flat inner surface with the interface to the liquid from where it is reflected to a second elliptical mirror. This design avoids standing waves, which appear for parallel plate container walls, and also guaranties that the part of incoming radiation which is reflected from the outer air-PE surface does not reach the second elliptical mirror which focuses the reflected radiation from the liquid to the Josephson detector. After a critical examination of our previous quasioptical set-up for identification of bottled liquids [12], some factors, which might lead to less accurate measurements, were found. Beside the mentioned standing waves, the accuracy of the bottle positioning can have the largest effect on the result of measurements, especially at higher frequencies. To reach the identification limits imposed by the liquids themselves, we have used the new described PE-cell, where the liquids under study were filled and which was at a fixed position in the set-up during the change of liquids.

Finally, the reflected radiation enters an evacuated Al-container (6) through a guiding horn with absorbing coating and a wedged PE-window. Inside the container, the high- $T_c$  bicrystal Josephson junction together with the integrated log-periodical antenna and a Si-lens on top is placed on the cold finger of the Stirling cooler and protected by thermal radiation shields. For the measurements on different liquids we have used several frequency multipliers, which could deliver spectral lines at around 30, 100, 300, 350 and 450 GHz. The synthesized radiation was modulated at a frequency of 100 kHz. The response of the Josephson detector on the reflected radiation was measured by a lock-in amplifier. Two time constants of 1 ms and  $10\mu\text{s}$  were used with total measurement time of 5 and 0.05 seconds, correspondingly.

### 2.3. Measurements on various liquids

Due to a narrow, single-valued instrumental function, the developed Hilbert spectrometer gives us a possibility to use it in the case of complicated spectra, like polychromatic and continuous spectra. An example of the response  $\Delta I(V)$  of the Josephson detector to polychromatic radiation, consisting of three spectral lines which was reflected from PE-water interface in the cell, is shown in Fig. 2. Only three odd-symmetric resonances, corresponding to three spectral lines at the voltages corresponding to 261 GHz, 348 GHz and 435 GHz are observed in the response  $\Delta I(V)$ . Actually, in this set-up with well-defined spectral lines in radiation, we can use the detector response  $\Delta I(V)$  only to determine the reflectance from

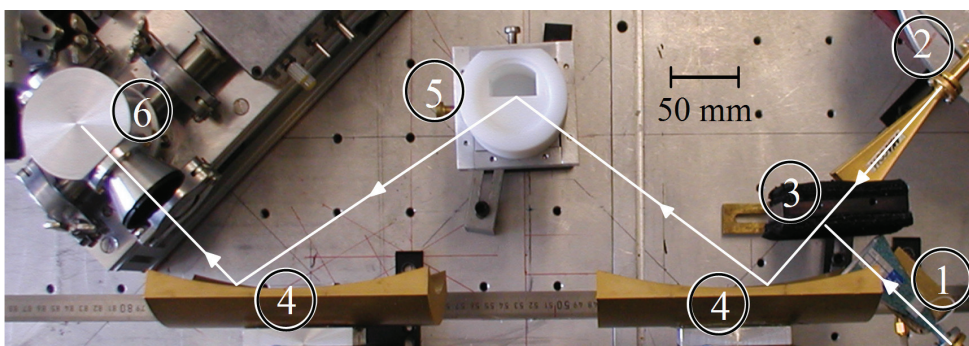


Fig. 3. Experimental setup: (1) low-frequency microwave source; (2) high-frequency microwave source; (3) beam combiner; (4) elliptical mirror; (5) polyethylene cell for liquid; (6) housing of Josephson junction detector with optical window on Stirling cooler.

the liquids, without converting measured data into a spectrum by Hilbert transformation. This approach allows us to avoid possible calculation errors and speed up identification process. Also, in measurements on many different liquids with rather different reflections shown in Fig. 4, we use water as a reflection reference because this liquid is the most intensively studied one and it is one of the recommended reference substances [13].

The reflection from the 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solution, which can act as an oxidizer for liquid explosives, was studied more carefully as its dielectric function is very close to the dielectric function of water (see Fig. 1). The liquids were changed without moving the cell to reduce possible errors due to taking out and inserting in the cell. During the experiment, the 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solution was replaced by water and back 10 times and the time between the liquid changes was reduced to about 10-15 seconds. A noticeable difference in the reflection from the water and the 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solution was first observed only at frequency of 282 GHz. The value of average reflection was calculated from ten serial measurements of water. The average reflection from the 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solution was calculated to be of  $1.017 \pm 0.003$  at 282 GHz. The reflectance values for the 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solution at lower frequencies of around 30 and 100 GHz were found to be practically undistinguishable from the corresponding values for pure water. So, we have extended the frequency range of our measurements to higher frequencies and carried reflectance measurements at 261, 348 and 435 GHz lines with a new frequency multiplier from RPG [11].

The results are presented in Fig. 5, where we can see an increase of relative reflectance from 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solution with the frequency from the value of 1.017 at 282 GHz to 1.033 at 434 GHz. It follows from these data that diluted water solutions of hydrogen peroxide are characterized the same dielectric properties as water at frequencies below 100 GHz and their dielectric properties at higher frequencies 300-450 GHz might be around 3% higher in comparison with that of water.

In a simple Debye model of liquids, the dielectric function  $\epsilon(f)$  is described by  $\epsilon(f) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + i \cdot 2\pi f\tau)$ , where  $\epsilon_\infty$  is the “infinite frequency permittivity”,  $\epsilon_0$  is the static dielectric constant and  $\tau$  is the relaxation time. Our data might indicate that the static constants  $\epsilon_0$  for diluted water solutions of hydrogen peroxide are very close to that of water within the accuracy of 0.3% and there are small differences of a few percent, in the values of  $\epsilon_\infty$  for 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  and pure water. Last circumstance can be used for optimizing the identification concept. Especially if the limiting frequency will be extended to higher values in future there is the chance to analyze additional shorter relaxation times which are characteristic

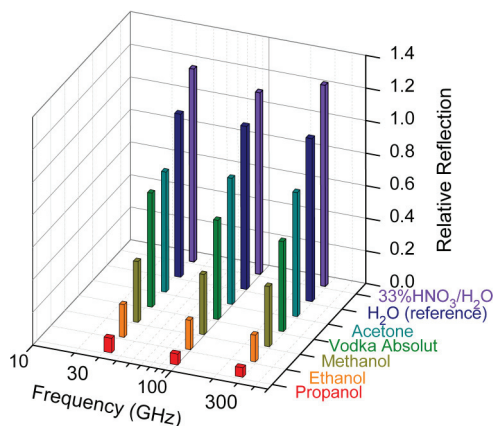


Fig. 4. Measured reflectance of various liquids at 31.8, 95.4 and 282 GHz normalized to water.

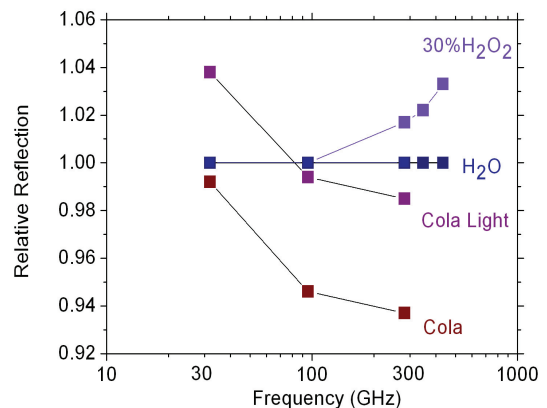


Fig. 5. Reflectance for  $\text{H}_2\text{O}$  and 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ . For comparison also typical benign beverage liquids are shown.

for many liquids. Furthermore, there is a development using dielectric waveguides under way [14] which might lead to improvements in comparison with the quasioptical approach. Especially one might avoid some problems like reflection from the bottle surface together with standing waves or positioning which can occur if commercial bottles instead of a special test cells are used.

### 3. Conclusion

We have developed a set-up for liquid identification based on polychromatic reflectance measurements by a high- $T_c$  Josephson frequency-selective detector, integrated on a Stirling cooler. After excluding errors, related with a positioning of various liquid sample, we were able to reach an accuracy of 0.3% for reflectance measurements.

A set of some relevant liquids, both benign and threat, have been measured and it was shown that identification of liquids, including diluted solutions of hydrogen peroxide in water, is possible by this technique, when measurements are extended to frequencies up to 450 GHz. Further improvements of the identifier are related with better power stability of oscillators, a guidance of the radiation completely within a dielectric waveguide and higher frequencies of the polychromatic source.

### Acknowledgements

This work was supported by Helmholtz Association of German Research Centers (project HRJRG-207) and Russian Foundation for Basic Research (project 11-02-91321-SIG\_a).

### References

- [1] Mostak P, Chemistry and Properties of Liquid Explosives. In: Schubert, Kuznetsov A, editors. *NATO Science for Peace and Security Series B*, Springer; 2008, pp 15- 25.
- [2] Existing and Potential Standoff Explosives Detection Techniques, Nat. Academies Press, Washington, D.C. 2004.
- [3] Divin Y Y, Polyanski O Y, and Shul'man A Y, *Sov Tech Phys Lett*. 1980; **6**:454.
- [4] Divin Y Y, Poppe U, Volkov O Y, and Pavlovskii V V. Frequency-selective incoherent detection of terahertz radiation by high- $T_c$  Josephson junctions. *Appl Phys Lett*. 2000; **76**:2826.
- [5] Divin Y, Volkov O, Pavlovskii V, Shirovov V, Shadrin P, Poppe U, Urban K. In: Krammer B. editor. Berlin: Springer. *Adv. Solid State Phys.*2001; **41**, pp 301-313.
- [6] Divin Y Y, Poppe U, Urban K. Hilbert spectroscopy of liquids for security screening. In: Schubert H, Kuznetsov A, editors. *NATO Science for Peace and Security Series B*, Springer; 2008; pp 189 – 204.
- [7] Divin Y, Poppe U, Gubankov V, Urban K. High- $T_c$  Josephson Detectors and Hilbert Spectroscopy for Security Applications. *IEEE Sensors J*. 2008; **8**, pp 750-757.
- [8] Gross P M and Taylor R C. The Dielectric Constants of Water, Hydrogen Peroxide and Hydrogen Peroxide-Mixtures. *J Amer Soc*. 1950; **72**, pp.2075-2080.
- [9] Volkov O Y, Pavlovskii V V, Divin Y Y, Poppe U. Far-infrared Hilbert-transform spectrometer based on Stirling cooler. In *Applied Superconductivity 1999*. In: Ed. Obradors X, Sandiumenge F and Fontcuberta J, *Inst. of Physics Conf. Ser. No.167, IOP Publishing Ltd., Bristol*. 2000; **2**, pp 623-626.
- [10] Divin Y , Lyatti M., Poppe U, Urban K. Hilbert spectroscopy based on the ac Josephson effect for liquid identification, *J. Phys.: Conf. Ser.* 2010; **234**:042005.
- [11] Radiometer Physics GmbH, Meckenheim, Germany.
- [12] Lyatti M, Divin Y, Poppe U, Urban K. Liquid identification by Hilbert spectroscopy. *Supercond Sci Technol*. 2009; **22**:114005.
- [13] Kaatze U. Techniques for measuring the dielectric properties of materials. *Metrologia*. 2010; **47**: pp S91-S113.
- [14] Liatti M, Poppe U, Divin Y. Josephson spectrometer with waveguide coupling for liquid identification; submitted to this volume.