„Detection of fluoro and chloro organics in traces by ultrasound pretreatment and ion chromatography"

Meeting of WG „Microwave and Ultrasound Activation in Chemical Analysis", COST D32 Chemistry

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Zentrum für Sorption und Reaktion

Content

1. Institut für Nichtklassische Chemie e.V. an der Universität Leipzig (INC)

objectives and aims, working groups, research profile

2. Characterization of ultrasonic fields

3. Application of ultrasound in the chemical technology and analysis (overview on actual and finished projects at the INC)

aquasonolysis

- **degradation of ozone by ultrasound irradiation in process water**
  → **ozone measurement techniques**
- **degradation of organic compounds by ultrasound irradiation**
  → **detection of halogenated pollutants in waste and industrial water**

mechanical action at liquid-liquid interfaces

- **phase transfer catalysis (preparation of biodiesel)**
- **emulsification**

mechanical action at liquid-solid interface

- **digestion of biomass in the biogas reactor**
- **cleaning and reactivation of catalysts in the heterogeneous catalytic oxidation of organic pollutants with H_2O_2 in waste water**

4. Conclusions

Institut für Nichtklassische Chemie e.V. an der Universität Leipzig

director:
Prof. Dr. H. Papp

managing director:
Priv.-Doz. Dr. R. Staudt

staff:
12 scientists and engineers

Working groups

- adsorption and high pressure processing (Priv.-Doz. Dr. R. Staudt)
- application of ultrasound and microwaves (Dr. J. Hofmann)
- high temperature processing (Dr. W. Zychlinski)
- chemical and isotope analysis (Dr. H.-M. Nitzsche)

Origin of ultrasound effects

1. Acoustic cavitation:

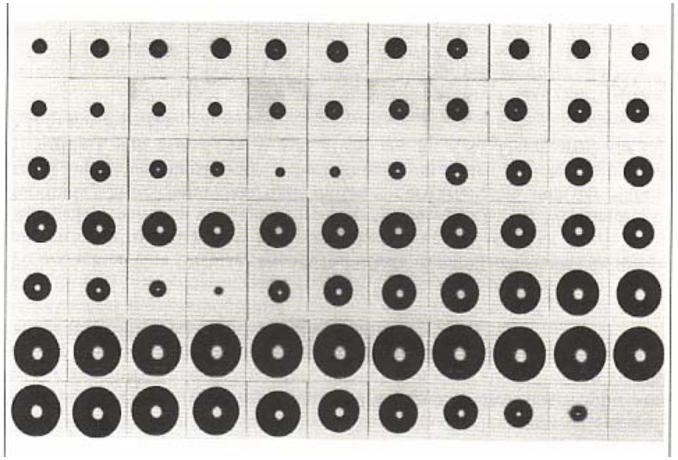
Formation and collapse of micro bubbles when ultrasonic waves are propagated in a fluid media.

The ultrasonic power density has to be higher than the cavitation barrier!

2. Pressure gradient:

Influencing the phase transfer processes at the phase boundary by micro streams generated by pressure differences.

With standing ultrasonic waves between reflector and transducer or between two transducers the separation of a suspension into a high density phase and an low density phase can be reached .



Cavitation of a laser-induced vapor bubble in silicon oil, 75.000 frames/sec (Lauterborn et al.)

Change of ultrasound and cavitation parameters with frequency

frequency of ultrasound	20 kHz	850 kHz
wavelength in water	≈ 70 mm	≈ 1.5 mm
radius of cavitation bubble	≈ 10 µm	≈ 0,3 µm
time of implosion of cavitation bubble	≈ 10^{-5} s	≈ 10^{-7} s
cavitation process	heat transfer to water phase	adiabatic implosion of cavitation bubble
influence on temperature and pressure	lower temperature and pressure	extreme high temperature and pressure
mechanical effects	powerful	average
transducer	horn, push-pull, bath	planar transducer
ultrasonic field	inhomogeneous	homogeneous
yield of OH-radicals formed from water in the cavitation bubble	average	high

Characterization of ultrasound

1. Power of ultrasound transferred into the fluid

- **calorimetry** (In a pure liquid all mechanical (ultrasound) energy produces heat and so, via calorimetry, some estimate of the output power can be obtained.)
- Fricke-dosimetry ($Fe^{2+} \rightarrow Fe^{3+}$)
- model reactions (radical scavenger, iodine-dosimeter)

2. Geometry of the ultrasonic field – setting up the ultrasonic system

- perforations in foil of aluminum
- temperature control (polymer pad with temperature sensor)
- hydrophone (scanning the reactor)
- sonoluminescence (intensity low)
- **chemoluminescense**

$\Downarrow$

- generation of reactive species by cavitation (OH-radicals; hydrogen peroxide)
- reaction with Luminol and emission of blue light
- the intensity of power ultrasound is proportional to brightness
- documentation of the ultrasonic field by photography (exposure time 30 seconds to one minute).

Microelectronic industry:
ozone measurement in the water phase

Problem:

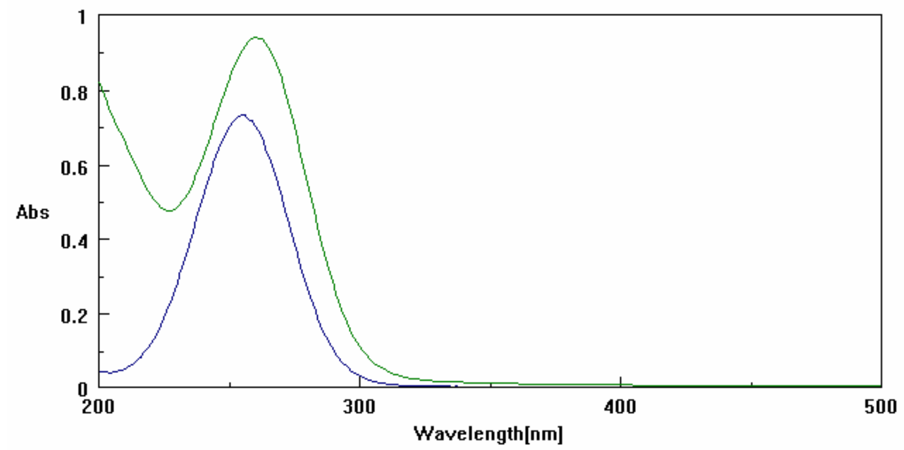
- **continuous detection of ozone to control processes in the metallurgy chemical industry, and in waste water treatment**
- **main application: microelectronic industry**

Idea:

- **UV-absorption of ozone at 254 nm (maximum of absorption spectra)**
- **The equipment can be installed in a bypass of a circulation water system.**

Equipment:

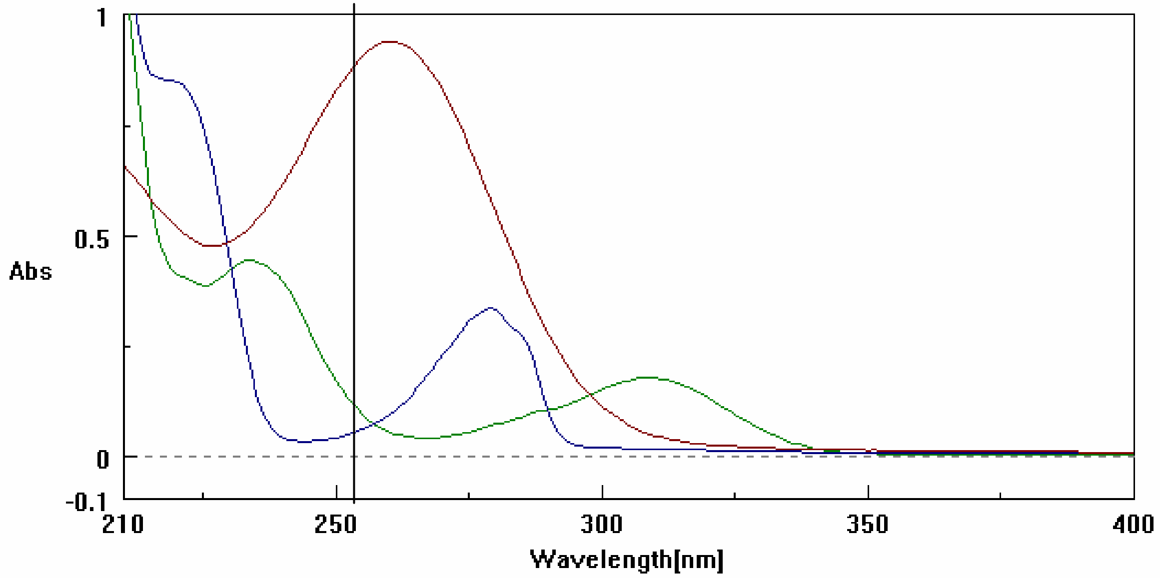
- **relative simple: UV-lamp, light pipe, detector**
- **absorption wavelength: 254 nm**
- **application of the gas phase equipment in the water phase**



Comparison of the spectra from ozone in water (green) and in air (blue)

Ultrasound in the ozone measurement 1 - problems to solve in the water phase

- **Organic compounds (e.g. nitrophenol, aniline) dissolved in water absorb at the same wavelength (254 nm).**
- **The equipment measures the sum of all compounds in the water.**
- **A correction of the signal is necessary!**
- **To get a „zero“-value the ozone has to be removed or degraded.**

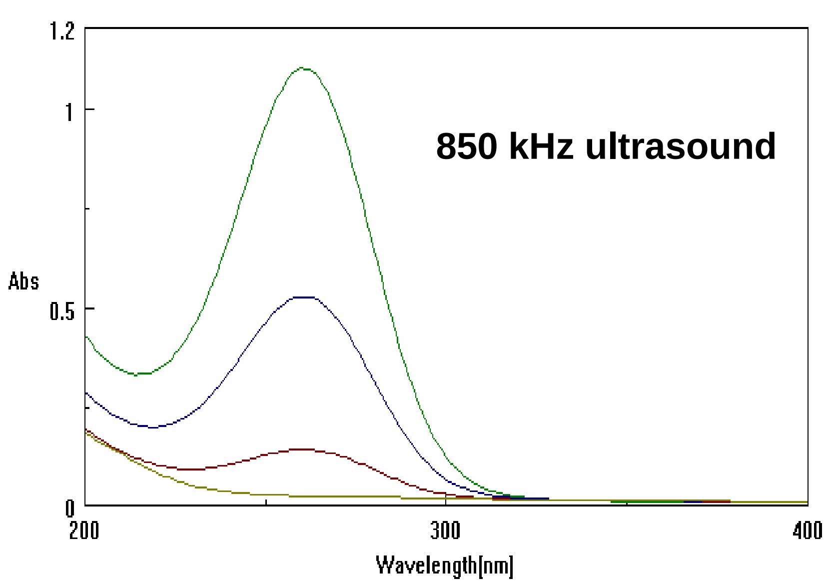


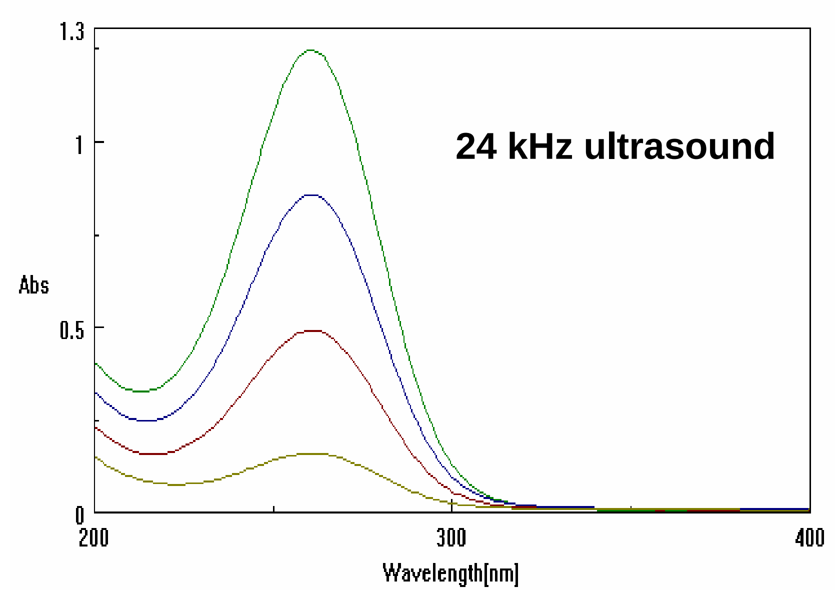
UV-spectra of ozone (brown), nitrophenol (green) and chlorohydroxyaniline (blue)

Ultrasound in the ozone measurement 2 - influence of frequency on the aquasonolysis of ozone

Degradation of ozone with 850 kHz (left) and 24 kHz (right) ultrasound:

reactor:	**cylindrical reactor; volume: 400 ml**
ultrasound:	**planar transducer (850 kHz) power: 50 W or ultrasonic horn (24 kHz), power: 50 W,**
ozone:	**water saturated with ozone (start)**
UV-spectrometer:	**Jasco V-530**

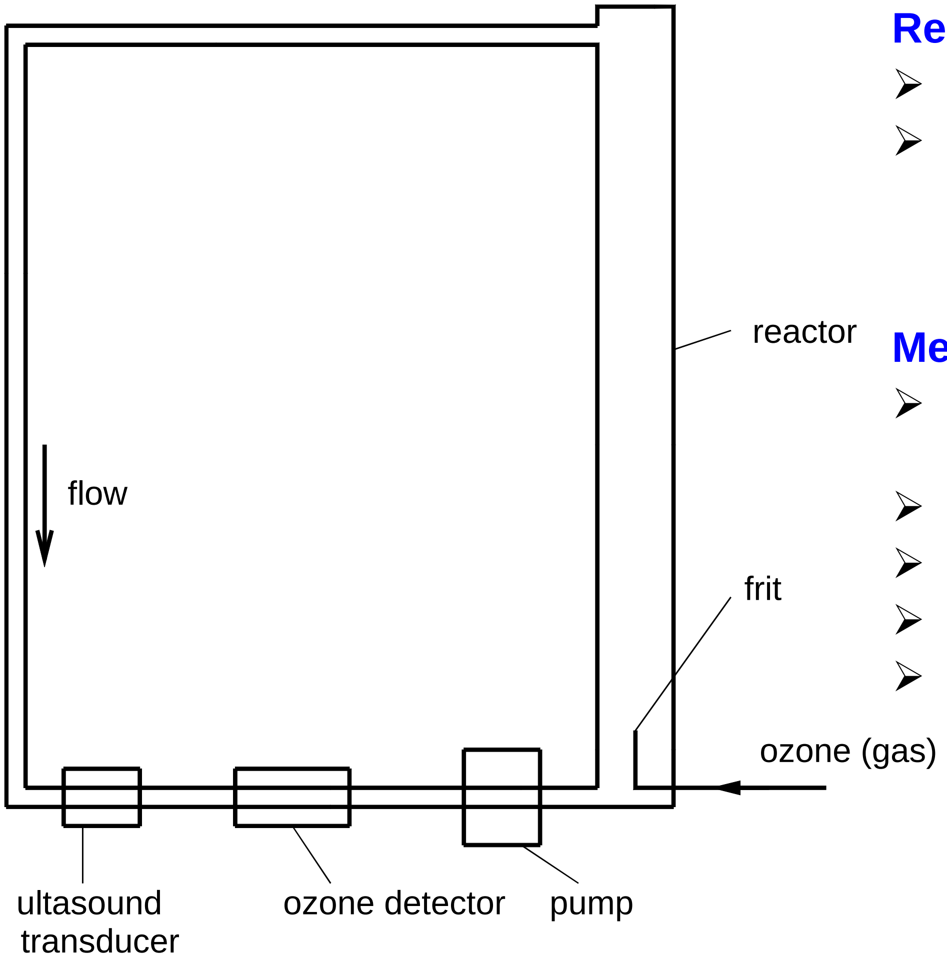




green: start; blue: 1 min; brown: 3 min; yellow: 7 min

The degradation rate of ozone is with 850 kHz higher than with 24 kHz!

Ultrasound in the ozone measurement 3 - first test with the own equipment in a circulation system



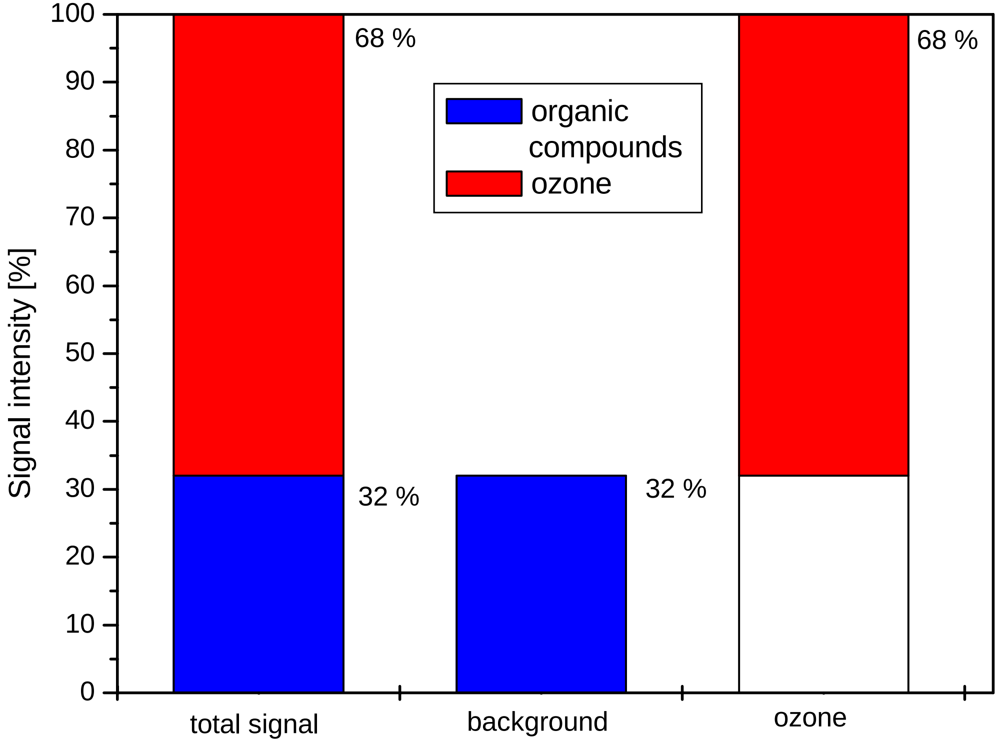
Reactor:

- reactor volume 3L;
- saturation of water inside the reactor with ozone by a gas stream from a ozone generator;

Measurement:

- circulation water system (bypass; pump flow: 100 to 500 mL/min);
- phase 1: without ultrasound;
- phase 2: with ultrasound;
- phase 3: without ultrasound;
- pseudo continuously detector.

Ultrasound in the ozone measurement 4 - measuring



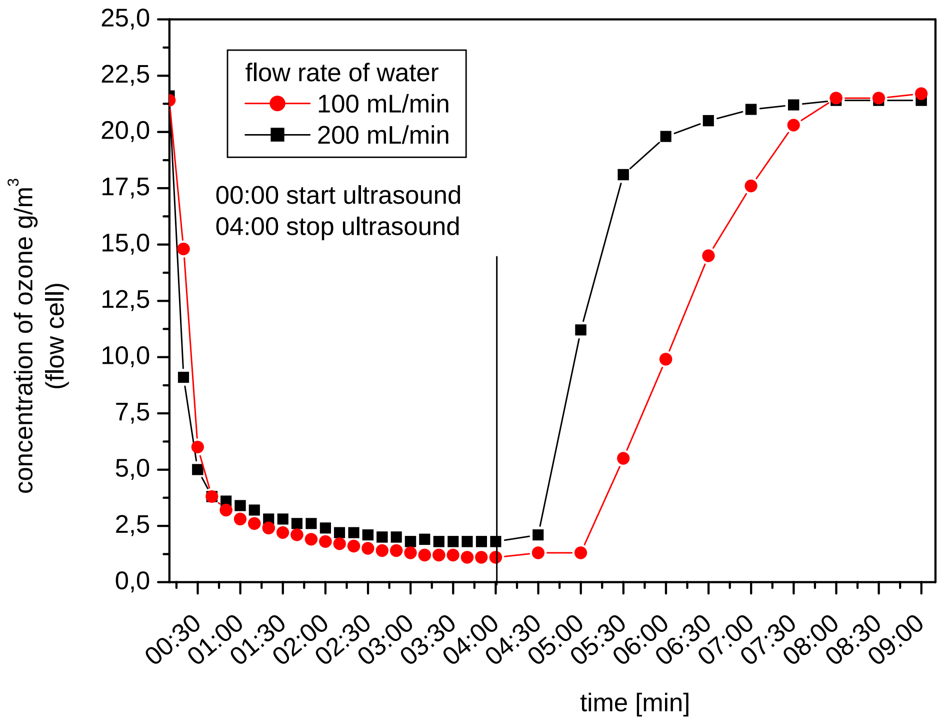
Measuring result

- ✓ **phase 1: total absorption (organics and ozone)**
- ✓ **phase 2: absorption of organics**
- ✓ **phase 3: total absorption (organics and ozone)**
- ✓ **difference: ozone**

The process will be repeated up to 10 phases.

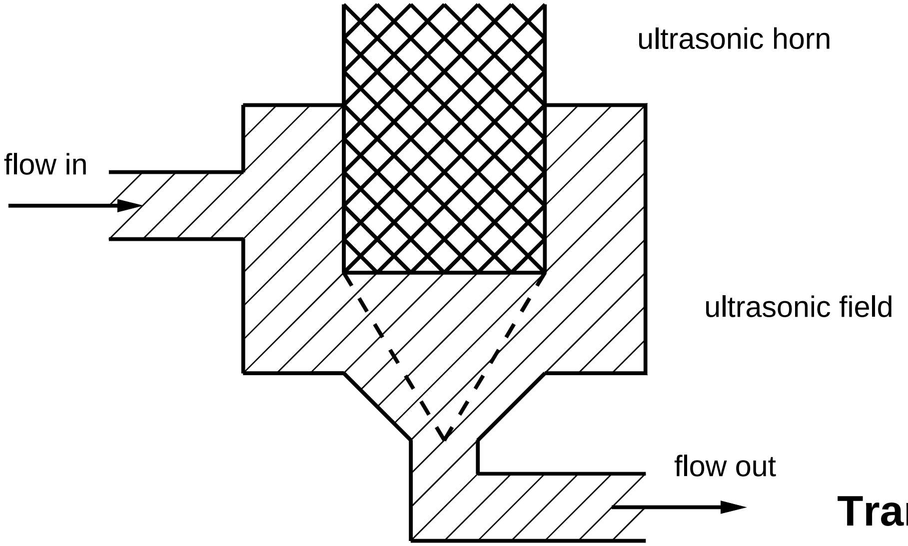
→ Identification of drifting effects

Ultrasound in the ozone measurement 5 - results of the measurements



- **Ultrasound 24 kHz in the flow cell before the ozone detector degreases > 95 % of the ozone dissolved in water!**
- **3 minutes after the start of the ultrasound the measuring signal is at the minimum level.**
- **Detection and the "zero"-value is possible.**
- **From the difference between the maximum level in phase 1 and 3 and the minimum level in phase 2 the ozone concentration can be calculated!**

Ultrasound in the ozone measurement 6 -
Ultrasonic field of ultrasonic horn used in the detector



Transducer manufactured by Hielscher, Germany, (500 W, 24 kHz) equipped with a ultrasonic horn diameter: 10 to 50 mm)

high intensity ultrasound in a small volume

Detection of ultrasonic field: chemoluminescense of Luminol in water.
high intensity: white (light blue) areas; low intensity: black areas

Ultrasound in the ozone measurement 7 - portable measuring equipment

Preproduction model, prototype

Measuring equipment can be used:

- in the bypass (installed in the technical equipment)
- portable kit (bag format)

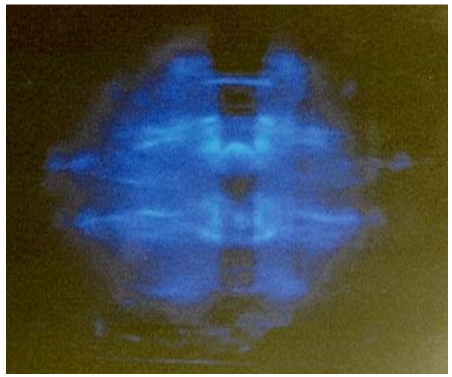
Necessary for the measurement:

✓ electric power (220 or 110 V)

✓ adapter to the water system (hose-connecting point)

Ultrasonic field of push pull transducers
(measured by chemoluminescense of Luminol in water)

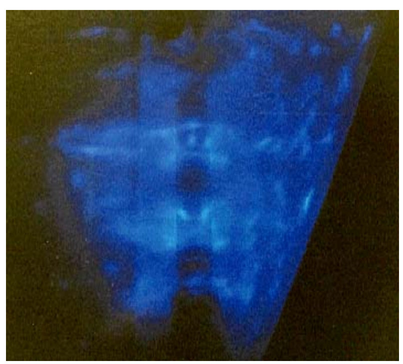
Push-pull-transducer manufactured by Walther, Germany, (600 W, 25 kHz)

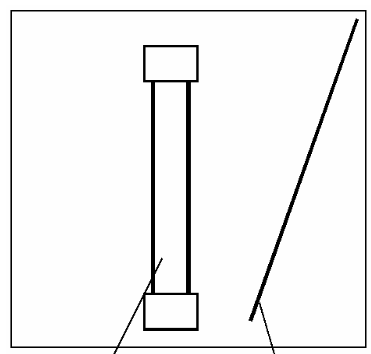


diameter: 50 mm
length: 300 mm

- **two planes with high intensity (depending on oscillation geometry of the rod)**

Ultrasonic field (25 kHz) near a wall

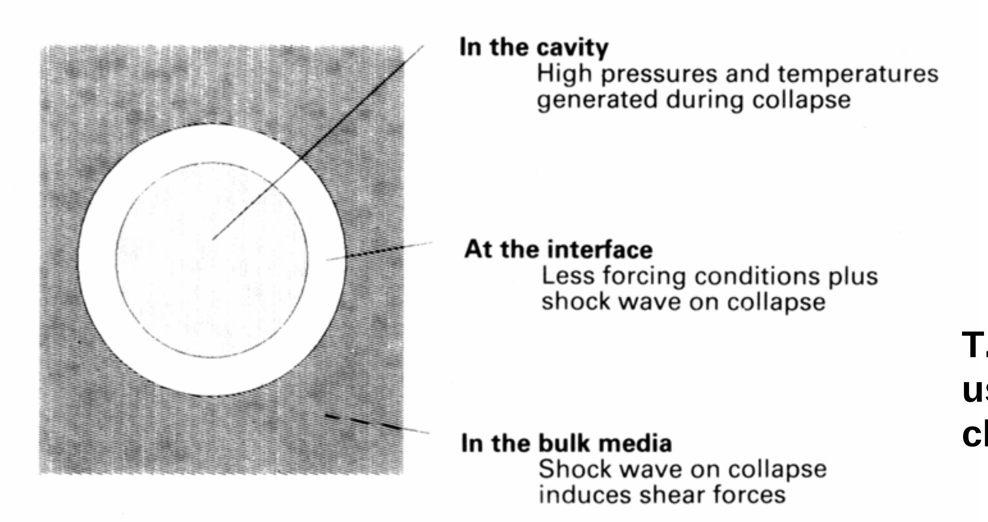




transducer **wall (glass or metal)**

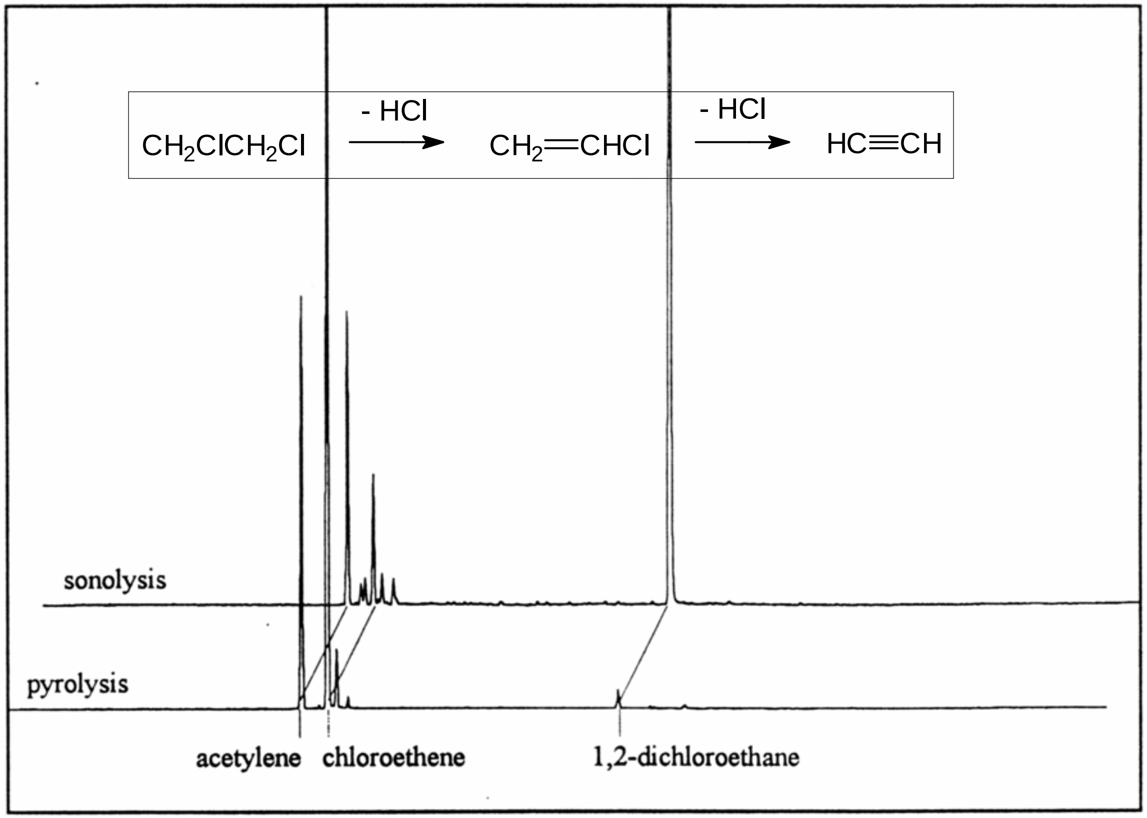
Degradation of organic compounds by ultrasound irradiation

- **Pathways for the degradation of organic compounds by ultrasound irradiation**
  - **in the cavitation bubble by thermal and thermal oxidative reactions (low boiling point, low polarity; fast)**
  - **at the interface**
  - **oxidation processes by OH-radicals or hydrogen peroxide (high boiling point, high polarity; slow)**



T. J. Mason: „practical sonochemistry – user‘s guide to applications in chemistry and chemical engineering“

Product formation in the aquasonolysis in the thermolysis of 1,2-dichloroethane



aquasonolysis: 100 mg/L Dichloroethane in pure water, 3 min sonication time, frequency 850 kHz

pyrolysis: 800 °C, 0.3 s, flow system, diluent gas: nitrogen

Result:

In the aquasonolysis and in the thermolysis vinyl chloride and acetylene are formed as main products from 1,2-dichloroethane.

-In the catalytic oxidation (driven by OH-radicals) other intermediates are formed:

-chloroethanol etc.

Conclusion:

The main reaction in the aquasonolysis of halogenated organic compounds is the thermolyse inside the cavitation bubble!

Detection of halogenated organic compounds in water

Halogenated organic compounds (fluoro-, chloro-, and bromo-organics) are used in the refrigeration engineering and in the dry-cleaning.

They are found in the environment (dry-cleanings, dumps, ground water, in the soil etc.)

Volatile chlorinated compounds can be detected by gas chromatography in combination with flame ionization detector or electron capture detector.

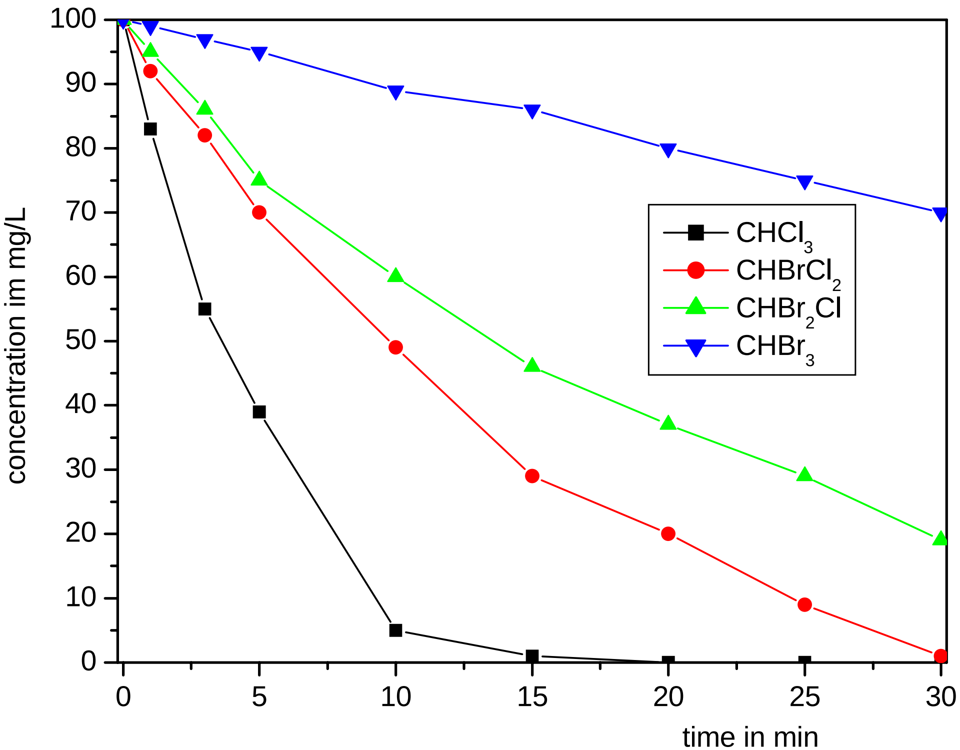
Standards are necessary for the calibration of the analysis.

No direct information on the content of chlorine, fluorine and bromine in organic compounds dissolved in the water are available.

Idea:

Degradation of halogenated organic compounds by ultrasound and ion chromatography.

Degradation of haloforms with ultrasound irradiation



Comparison of the degradation of haloforms (850 kHz, planar transducer, 100 mg/l)

Investigated compounds:

- **chloroform,**
- **bromodichloromethane,**
- **dibromochloromethane,**
- **bromoform.**

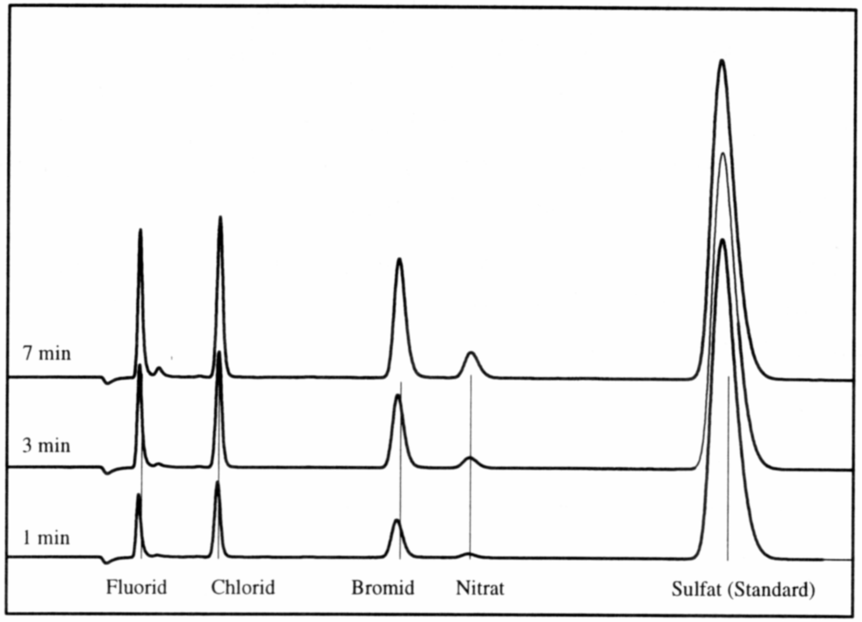
The haloforms were totally transformed to carbon oxides, hydrochloric and/or hydrobromic acid.

results:

Fluoroorganics are degraded with high reaction rate.
With increasing content of halogenes in the organic compound the degradation rate decreases.
Bromoorganics react slowly.

Chlorinated and fluorinated organic compounds can be degraded with 850 kHz ultrasound in few minutes (complete conversion: 15 min; 20 W power).

Degradation of dibromochlorofluormethane



Ion chromatography

- **ion chromatograph DX 100 (DIONEX GmbH)**
- **column: AS12A, 4 mm; eluent: 2,7 mmol/L Na_2CO_3 / 0,3 mmol/L $NaHCO_3$).**

Aquasonolysis:

– **room temperature;**

– **50 mg/l dibromochlorofluoromethane**

– **850 kHz planar transducer, Meinhardt Ultraschalltechnik Leipzig, 100 W power;**

– **10 ml headspace vials.**

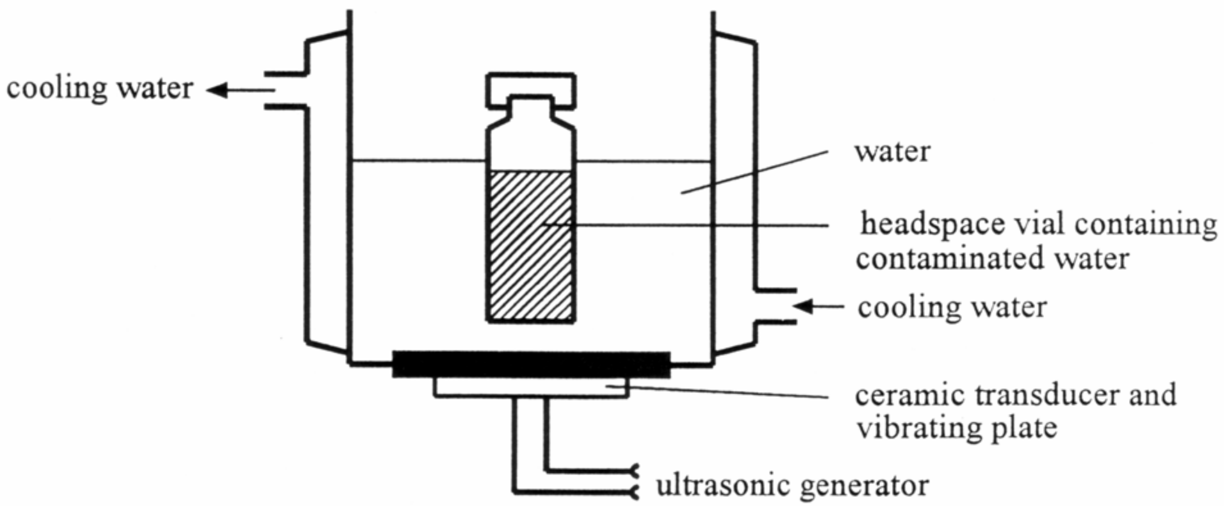
Result:

– **HF, HCl and HBr are formed in parallel in the ration 1 : 1 : 2.**

–**The degradation is complete in 7 minutes.**

$$CFClBr_2 \xrightarrow{H_2O} CO_2 + HF + HCl + 2\ HBr$$

Degradation of halogenated organic compounds - equipment and ultrasonic field



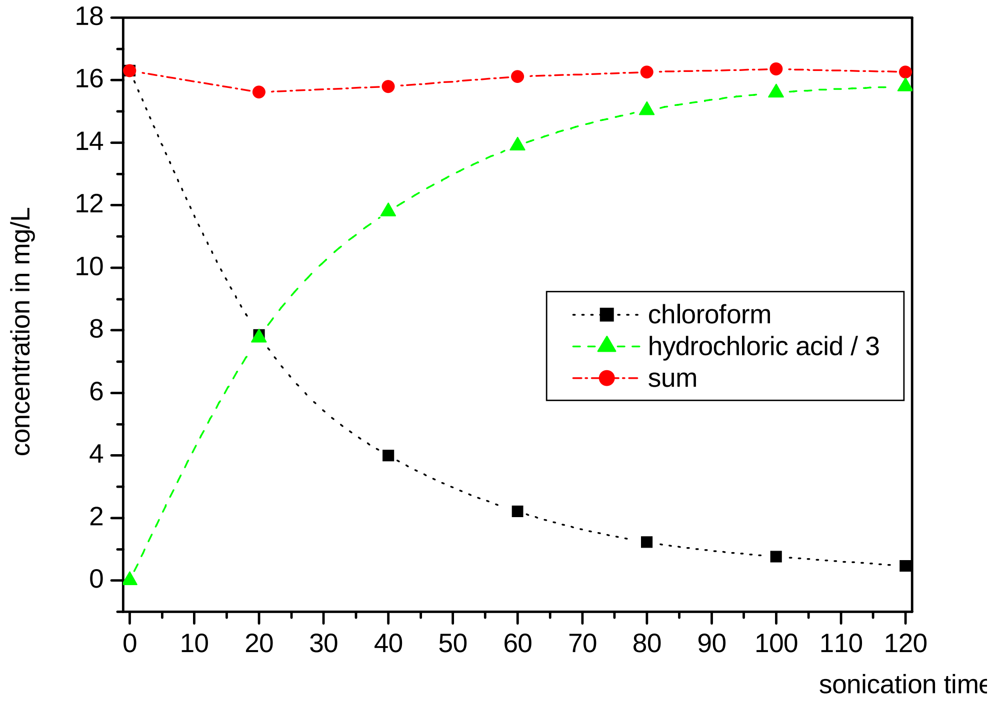
reactor for the degradation of halogenated organic compounds in the 10 ml scale (headspace vial)

ultrasonic field

(detected by chemoluminescence)

For the degradation vials from special glass material must be selected to guarantee the penetration of the water phase inside the vial.

Degradation of halogenated organic compounds - comparison headspace gas chromatography and sonolysis / ion chromatography



$$CHCl_3 \xrightarrow{H_2O} CO_x + 3\ HCl$$

Example:

Degradation of trichloromethane (Chloroform)

Chloroforme consumtion:

→ Headspace gas chromatography

Hydrochloric acid formation

→ Ion chromatography

Both methods give comparable Results!

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Conclusions

1. Ozone detection using ultrasound und UV-absorption

feasible, practicable

scale-down is successful finished

software development in process

2. Detection of halogenated organic compounds

practicable

tests with model water successful

problems with high concentrations of salts (NaCl, Na_2SO_4 etc.) in ground water

ion chromatography must be adapted and developed

Ultrasound is a powerful tool in the chemical technology and in analysis.

Under consideration of the properties of ultrasound a careful adaptation of the equipment has to be done.