Title: METHOD AND DEVICE FOR MEASURING THE CONCENTRATION, VISCOSITY AND SURFACE TENSION OF A SUBSTANCE USING A RESONATOR

Abstract: The present invention is related to the method and device for measuring the chemical and biological analyte or viscosity and surface tension of the liquid. The device is comprised of a tuning fork type quartz crystal resonator having an associated resonant frequency and the sensing part attached to at least one prong of the resonator. The sensing part is made from low density and high surface area material, e.g. carbon nanotube fibre. Method comprises the immersing of only the sensing part of the device into the liquid, excitation of the sensor with electric field and registration of the changes in resonant frequency due to changes in mass of the sensing part or due to changes in viscosity and surface tension of the liquid.

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Description

METHOD AND DEVICE FOR MEASURING THE CONCENTRATION, VISCOSITY AND SURFACE TENSION OF A SUBSTANCE USING A RESONATOR

Technical Field

[0001] The present invention relates to the field of sensorics, more precisely, to the field of measuring equipment of biological and chemical composition of fluids as well as viscosity and surface tension. The invention is related to the resonator, based on the quartz crystal, for example tuning fork type quartz crystal resonator (quartz tuning fork, QTF). The invention is primarily related to measuring fluids with high dielectric permittivity, using a sensor based on quartz crystal.

Background Art

[0002] Quartz resonators are widely used for measuring very small concentrations of substance and their changes and viscosity and surface tension of the environment. Measuring concentration, viscosity and surface tension is possible due to the fact that the natural frequency of piezoelectric material depends heavily on the viscosity of the environment and surface tension and on the mass that has been precipitated on the sensor or that has left it.

[0003] Resonator is made by depositing the electrodes onto the surface of the quartz crystal, so that the crystal is located between the electrodes. Two principal methods are used for measuring crystal's resonant frequency:
- mechanical excitation of the crystal and registering the resulting electric signal;
- electrical excitation of the quartz resonator by applying alternating voltage and registering the frequency at which the oscillation amplitude is maximal (so-called self-excitation mode).

[0004] Crystals of various shapes are used as resonators, for example tuning fork type crystal, which can be for example a quartz crystal that is used as a time standard in watches. Resonator with a shape of a tuning fork has certain advantages over other shape (e.g. plate-shaped) quartz crystals, for example low cost, high stability of the resonant frequency and good Q-factor.
[0005] The possibility to use the tuning fork type quartz crystal in the biosensor solution has been described experimentally [Xiaodi Su, Changchun Dai, Jian Zhang, Sean J. O'Shea, Quartz tuning fork biosensor, Biosensors 
Bioelectronics 17 (2002) 111-117]. In that described technical solution the surface of the crystal is covered with specific biomolecules, so that the resulting sensor reacts selectively only to the substance examined.

[0006] Also, it has been shown that the tuning fork type crystal can be used to investigate the properties of fluids, incl. viscosity [L. Matsiev, J. Bennett, O. Kolosov, High Precision TuningFork Sensor for Liquid Property Measurements, IEEE Ultrasonics Proceedings, Volume 3 (2005) 1492-1495]. This document describes a solution in which quartz tuning fork is immersed directly into the investigated fluid demonstrating that resonant frequency depends on the density and viscosity of the fluid. The dependence of the fluid's surface tension on the viscosity has been shown in [A.H. Pelofsky, Surface Tension-Viscosity Relation for Liquids, Journal of Chemical and Engineering Data 11 (1966) 394-397].

20.09.2007 describes a tuning fork type quartz crystal being used in preparing a bio- and chemical sensor, so that between the prongs of the tuning fork and perpendicular to the prongs a polymer fibre is attached, which has been made from such a material or modified in such a manner that the sensor reacts selectively only to a certain investigated material.

[0008] The abovementioned methods and respective and other known tuning fork type sensors have all one essential common disadvantage:
- sensors can be used either only in vacuum, gas atmosphere or organic solutions, because the tuning fork construction and location of electrodes does not allow using the sensor in fluids with high dielectric permittivity, for example in water, because a so-called "capacity effect" occurs and the tuning fork resistance drops not only at resonant frequency but also at all other frequencies.

[0009] Thus, determination of the resonance is virtually impossible. Whereas, covering the sensing part of given sensor with an isolated substance does not allow solving given problem as the effect is related to the electric field,
not to the movement of electrons. However, very many essential biological
and chemical reactions take place only in aqueous solutions. Therefore,
there exists no simple and inexpensive sensor that would allow performing
the abovementioned measurements in fluids with high dielectric
permittivity.

Disclosure of Invention

[0010] The aim of the present invention is to develop the method for chemical
analysis and investigation of fluid's viscosity and surface tension qualities,
which is based on a tuning fork type resonator, whereas the additive's
concentration and viscosity and surface tension sensor works also in fluids
with high dielectric permittivity, e.g. water. Also, current invention aims to
provide a sensor with simple structure, which can be employed in
implementing given method in fluids with high dielectric permittivity.

[0011] Method for measuring chemical and biological concentration of the
investigated substance and viscosity and surface tension qualities, which
includes attachment of the sensing part to the quartz tuning fork resonator,
immersing the sensing part of the sensor into the examined environment,
electric vibration of the sensor on a resonant frequency and feedback of
the changes of the resonant frequency, differs from the currently known
solutions in that additive and viscosity and surface tension sensing part of
the sensor is immersed into the fluid, whereas part of the resonator that is
covered with electrodes is kept above the fluid. Chemical, physical and
biological interaction between the sensing part of the sensor and the
examined substance in the fluid leads to the change of mass of the sensor
(increases for example in case of adsorption or immobilisation and
decreases for example with decomposition reaction). The change of mass
of the sensor's sensing part evokes the change in the sensor's resonant
frequency, which is registered electrically and is after that displayed as a
measuring result onto the screen of the measuring device. Resonant
frequency of the sensor depends also on the density, viscosity and surface
tension of the liquid it immersed in. It enables to perform measurements of
concentration, viscosity and surface tension in fluids with high dielectric
permittivity.
[0012] The device necessary for providing the method of the invention is a sensor, which comprises at least one tuning fork type quartz crystal having two prongs, an electric excitation system and recorder of frequency response, which is characterised by that the part immersible into fluid, so-called sensing part, is attached to one or both prongs of the resonator, so that sensing part acts as the extension of the prongs, preferably in the longitudinal direction of the prongs. The junction between the immersed part and the prong of the tuning fork needs to be rigid in order to prevent vibration losses between the tuning fork and sensing part of the sensor. The sensing part acting as the extension of the prongs is produced from a material with high specific surface area, e.g. nanoporous fibre, in order to obtain more points of adsorption / desorption and get stronger signal. For achieving the sensor's selectivity, fibre's surface is modified according to the investigated substance. Fibre needs to be rigid, so that it could be immersed into the fluid also when its density is lower than fluid's density. At the same time, it is not required that fibre would be located in the fluid straight and vertically. The minimum length of the fibre is chosen so that the registered signal would be the highest. It depends on the ability of the fibre to react with the investigated environment. However, maximum length of the fibre is not critical, as the maximum amplitude of the vibration in the fluid, created by the resonator, lies at the point of contact of fibre and surface of the fluid and it fades out as the immersion depth increases. Thus, measured signal will not increase significantly beyond certain fibre length and using longer fibre will not be justified. For example, using nanotube fibre with a diameter of 50 µm on a length exceeding 20 mm will not increase the signal.

[0013] For determining the chemical and biological concentration of the analysed substance the sensing part (fibre) of the sensor is immersed into a fluid where a reaction takes place, for example adsorption of the investigated substance or immobilisation onto fibre or decomposition reaction of the substance applied to the fibre, resulting in the change of mass of the sensor's sensing part. The change of fibre's mass causes change in the sensor's resonant frequency, which is then registered electrically. If the
immersible part (fibre) is of porous structure, it absorbs fluid in the solution, which results in changes of the fibre’s mass and sensor’s resonant frequency. Thus, if respective reaction is fast (faster than the time of sensor’s resonant frequency stabilisation in the fluid), then the fibre will be put initially in the clean solution until the frequency would stabilise and immediately afterwards it would be placed in the investigated solution. If chemical or biological interaction is slow (several times slower than the time of sensor’s resonant frequency stabilisation in the fluid), then the sensor’s sensing part would be immersed directly into the investigated fluid and resonant frequency change in time would be registered, based on which the reaction kinetics can be examined. Sensor’s depth below the fluid level depends on the hydrophilicity or hydrophobicity of the sensor’s immersed part. The greater the hydrophilicity of the sensor’s sensing part, the farther away should the electrodes remain from the fluid level, so that fluid could be prevented from getting onto electrodes. Device sensitivity decreases on the occasion unreasonably long distance.

[0014] The sensing part (without electrodes) of the sensor attached to it is immersed into a fluid to measure fluid viscosity. Using resonant frequency difference between various viscosity and surface tension standards and the investigated substance, viscosity and surface tension of the investigated fluid is determined.

**Brief Description of Drawings**

[0015] The present method according to the invention and the device needed for its implementation is described in more detail in following exemplary embodiments with references to annexed figures where:

[0016] Fig 1 illustrates the sensor with one sensing part (fibre) of the device according to the invention,

[0017] Fig 2 illustrates the sensor with two sensing parts (fibres) of the device according to the invention and schematic characteristics of the amplitude decrease,

[0018] Fig 3 illustrates measurement scheme according to the method of the invention,

[0019] Fig 4 illustrates the result of the experiment of attaching BSA (bovine
serum albumin) to the sensing part (fibre) of the device according to the invention;

[0020] Fig 5 illustrates the result of the viscosity and surface tension change experiment, which has been performed according to the method of the invention.

**Best Mode for Carrying Out the Invention**

[0021] Exemplary embodiments of the method

[0022] Example 1

Method for investigating protein adsorption kinetics, which included immersing the sensing part of the sensor into a fluid, vibration of the sensor on a resonant frequency by electrical excitation and feedback of the changes in resonant frequency. The sensor is made by gluing nanotube fiber with length of 20 mm and diameter of 50 µm longitudinally to one prong of tuning fork type quartz resonator having nominal frequency of 32768 Hz (Fig. 1). Bovine serum albumin (BSA) was selected as the attached protein. Method included the following steps:

a) two BSA solutions with a concentration of 0.1 mg/ml 5mM in phosphate buffer were prepared, one at pH7 and the other at pH4.8;

b) sensing part of the sensor was immersed into clean phosphate buffer into the depth of 18 mm and the resonator part, which was covered with electrodes, was maintained above the fluid;

c) electrical excitation was switched on and decrease of resonant frequency by 5 Hz due to the fluid absorption was registered;

d) after stabilisation, the sensor was placed into BSA solution at pH7 and the decrease of resonant frequency in time was registered, which was 4.5 Hz during 25 minutes;

e) the sensor was then placed back into clean buffer at pH7 in order to control whether the reaction was reversible or not; frequency did not change, which means that the reaction was irreversible;

f) procedure was repeated at pH4.8 and decrease of resonant frequency by 20 Hz was registered (Fig 4), which is around 4 times greater than at pH7 and conforms with the theory and results of other methods (L.E. Valenti, P.A. Fiorito, CD. Garcia and CE. Giacomelli, The
[0024] **Example 2**

[0025] Method for investigating the fluid viscosity and surface tension, which included immersing the sensing part of the sensor into a fluid, vibration of the sensor on a resonant frequency by electrical excitation, adding substance altering the viscosity and surface tension and feedback of the changes in resonant frequency. The sensor is made by gluing nanotube fiber with length of 20 mm and diameter of 50 µm longitudinally to one prong of tuning fork type quartz resonator having nominal frequency of 32768 Hz (Fig 1). Bovine serum albumin (BSA) solution was selected for investigating the fluid viscosity and surface tension. Method included the following steps:

a) sensing part of the sensor was immersed for saturation into 0.1 mg/ml BSA solution in phosphate buffer at pH4.8 (the aim of that step was to saturate the sensing part (fibre) with the substance (BSA) that adsorbed there);

b) following the stabilisation, the sensor was placed into clean phosphate buffer (pH 4.8, total volume 2 ml) into the depth of 18 mm while the resonator part, which was covered with electrodes, was maintained above the fluid;

c) electrical excitation was switched on and resonant frequency (31979 Hz) and amplitude (156.25 mV) were determined;

d) 300 mg of BSA was added, so that the final BSA concentration was 150 mg/ml;

e) resonant frequency (31995 Hz) and amplitude (228.55 mV) were determined once more, which is ca 1.5 times higher than prior to the addition of BSA. (Fig 5).

[0026] The device required for implementing the method comprises a resonator based on a quartz crystal, electric excitation system and resonant frequency recorder. Tuning fork type quartz crystal is chosen as the resonator. Sensing part with high specific surface area is attached to the end of one of the fork's prong, with its one end being connected to the
prong and the other being free (Fig 1).

[0027] Fig 1 illustrates a device for implementing the method according to the invention, which comprises a sensor with one sensing part (fibre), which has contacts 1, quartz resonator 2, electrodes deposited to the quartz resonator 3 and nanoporous fibre 4 or sensing part of the sensor.

[0028] Fig 2 illustrates a device according to the invention, which comprises a sensor with two sensing parts (fibres), which has contacts 1, quartz resonator 2, electrodes deposited to the quartz resonator 3 and nanoporous fibres 4 or sensing parts of the sensor attached to the ends of resonator prongs. Also, Fig 2 illustratively displays the schematic characteristics of the amplitude decrease.

[0029] Fig 3 illustrates a scheme of measurement according to the method of the invention, in which sensor's contacts 1 are connected to the generator, quartz resonator 2 with electrodes 3 deposited to it is located above the fluid containing the examined substance 5 and sensing parts of the sensor, which have been attached to the ends of the quartz resonator 2 of the sensor 1, nanoporous fibres 4 have been immersed into the fluid containing the investigated substance.

[0030] Sensing part is the extension of the prong, placed preferably in the longitudinal direction of the prong; however, the sensing part can be directed also at another angle with respect to the axis, which ensures the immersion of the sensing part into the investigated fluid, for example into a fluid with high dielectric permittivity like water (dielectric permittivity 34-88, depending on the temperature). The fluid with high dielectric permittivity comprises also electrolytes.

[0031] The junction between the sensing part and the prong is rigid in order to prevent vibration losses between the resonator fork and the sensing part. Sensing part is made of fibre material, which can be for example nanotube fibre prepared by dielectrophoresis or glass fibre onto which nanotubes have been grown for increasing the fibre’s specific surface area. Immersing only the sensing part of the sensor into the investigated fluid enables to use the method for fluids with high dielectric permittivity, which is impossible in case of immersing the prongs of quartz tuning fork.
because of short circuit of the electrodes deposited on prongs.

[0032] In the embodiment of the device according to the invention the sensing parts or fibres are attached to both prongs of the resonator, whereas sensing parts' one end, located away from the sensing part's attachment point on the fork's prong, is free and it is immersed into the fluid that is being investigated (Fig 2).'

[0033] In the further embodiment of the device according to the invention, the fibre parameters of sensing parts, which are being attached to both prongs of the resonator, e.g. material, rigidity, length, diameter, specific surface area, are the same and sensing parts are attached to the prongs so that they are both guided in the same direction, preferably in the longitudinal direction of the resonator prongs.

[0034] Exemplary embodiments of the device

[0035] Example 1

[0036] Device according to the invention for measuring chemical and biological concentration of the substance and viscosity comprises a tuning fork type quartz crystal with resonant frequency 32768 Hz, whereas a part that is immersed into fluid is attached onto one of its prongs, so that it acts as the extension of the prongs, preferably in the longitudinal direction of the prongs (Fig 1), while the point of attachment is rigid in order to prevent vibration losses between the tuning fork and the sensing part. The part acting as the extension of the prongs is with high specific surface area (e.g. nanoporous fibre), so that the measured signal would be greater.

[0037] Example 2

[0038] A sensing part that is immersed into fluid is attached onto one prong of the tuning fork type quartz crystal with resonant frequency 32768 Hz, so that it acts as the extension of the prong, preferably in the longitudinal direction of the prong (Fig 1), while the point of attachment is rigid in order to prevent vibration losses between the tuning fork and the sensing part. The part acting as the extension of the prong is of high specific surface area in order to increase sensitivity (e.g. nanoporous fibre) and its surface is modified (e.g. with a substance comprising carboxyl groups or streptavidin) in order to get greater selectivity with regard to the
investigated substance.

[0039] Example 3

[0040] A sensing part that is immersed into fluid is attached onto one prong of the tuning fork type quartz resonator with resonant frequency 32768 Hz, so that it acts as the extension of the prong, preferably in the longitudinal direction of the prong (Fig 1), while the point of attachment is rigid in order to prevent vibration losses between the tuning fork and the sensing part. Nanotube fibre produced by dielectrophoresis, having diameter of 50 µm and length of 20 mm is used as the extension of the prong. Fibre density is 0.5 g/cm³, tensile strength is 20 MPa, Young module is 1.5 GPa, and the fibre has nanoporous structure. Fibre is glued (e.g. with epoxide glue) to one prong of the fork along its direction.

[0041] Example 4

[0042] A part that is immersed into fluid is attached onto both prongs of the tuning fork type resonator, and having the resonant frequency of 32768 Hz, so that it acts as the extension of the prongs, preferably in the longitudinal direction of the prongs (Fig 2), while the point of attachment is rigid in order to prevent vibration losses between the tuning fork and the sensing part. The part acting as the extension of the prongs is of high specific surface area in order to increase sensitivity (e.g. nanoporous fibre) and its surface is modified (e.g. functionalised with specific molecules or covered with a specific substance) in order to get higher selectivity with regard to the investigated substance.

[0043] It will be readily understood by those skilled in the art that implementing the method according to the invention presented in the description of the invention and performing of measurements and examples of the device structure are not limiting the nature of the invention and scope of the protection of the invention determined by the incorporated claims, rather, the embodiment examples are provided by way of illustration.
Claims

1. The method for measuring chemical and biological concentration of the substance and viscosity and surface tension, whereby the sensing part of the sensor is immersed into the examined fluid, after which an electric signal is given/directed to the sensor, as a result of which vibration of the sensor is generated on a resonant frequency and thereafter changes of the resonant frequency due to changes in the mass of the sensor are registered, which is characterised by that the sensing part of the sensor is immersed partially into the fluid that is being examined, whereby the part covered by the resonator electrodes is left above the examined fluid.

2. A method according to claim 1, characterised by that the sensing part of the sensor is immersed into the examined fluid with high dielectric permittivity, which comprises also electrolytes.

3. A method according to claims 1 and 2, characterised by that the gap between the sensing part of the sensor, which is attached to the part of the resonator covered with electrodes, point of attachment and level of the fluid, shall be chosen according to wetting the sensing part of the sensor so that the meniscus of the examined fluid remains below the electrodes deposited on the quartz resonator.

4. A method according to claims 1-2, characterised by that the resonator is covered with hydrophobic substance prior to being immersed into the examined fluid in order to guarantee minimal gap between the point of attachment, located on the sensing part of the sensor of the resonator covered with electrodes, and the level of the fluid, increasing thereby the sensitivity of the equipment.

5. A method according to claims 1-4, characterised by that the reference method with regard to known standards is used for determining the concentration and viscosity and surface tension of substances, whereas immersion depth of the sensing part equals to measurement case.

6. A method according to claims 1-5, characterised by that for determining the concentration and surface tension of substances, preferably biological additives, the surface of the sensing part of the sensor is modified by immobilising with corresponding additives, so that the sensor reacts to a given
substance in an investigated environment.

7. A method according to claims 1-2, characterised by that, if the chemical or biological interaction with sensing part of the sensor is slow, the sensing part of the sensor is immersed into the examined fluid and the change in time of the sensor's resonant frequency is registered for investigating the reaction kinetics.

8. The device for measuring chemical and biological concentration of the substance and viscosity and surface tension for implementing the method according to claims 1-7, whereby the device comprises a resonator based on a tuning fork type quartz crystal, onto the prongs of which electrodes (3) are deposited, electric excitation system and recorder of resonant frequency, which is characterised by that a sensing part (4) with high specific surface area is attached to at least one prong of the quartz resonator (2), one end of that part being attached to the prong of the resonator and the other being free, so that the sensing part (4) is the extension of the resonator (2) prong, preferably in the longitudinal direction of the prong, whereby the point of attachment of the sensing part (4) on the prong of the resonator is rigid, which prevents vibration losses between the resonator fork and the sensing part.

9. A device according to claim 8, characterised by that the sensing part (4), which acts as the extension of the resonator prong, is made of fibre material.

10. A device according to claims 8 and 9 characterised by that the minimum length of the fibre is chosen so that measuring the signal gives maximum result.

11. A device according to claims 8 and 10 characterised by that the maximum length of the fibre is determined by the length, starting from which the measured signal does not increase.

12. A device according to claim 11, characterised by that the fibre material, which acts as the extension of the prongs, is a nanotube fibre prepared by dielectrophoresis.

13. A device according to claims 8-12, characterised by that the fibre material, which acts as the extension of the prongs, is glass fibre onto which nanotubes have been grown for increasing the fibre's specific surface area.

14. A device according to claims 8-13, characterised by that the sensing parts (4) are attached to both prongs of the resonator (2), so that one end of the sensing part (4), which is situated farther away from the sensing part's attachment point
with regard to the resonator (2) is free.

15. A device according to claims 8-14, characterised by that the fibre parameters of sensing parts (4) which are being attached to both prongs of the resonator (2), e.g. material, length, diameter, rigidity and specific surface area, are the same and that sensing parts are attached to the prongs so that they are guided in the same direction, preferably in the longitudinal direction of the resonator (2) prongs.
Fig. 2
Fig. 4

Fig. 5
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

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A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search

15 November 2010

Date of mailing of the international search report

07/12/2010

Name and mailing address of the ISA

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Authorized officer

Uttenthaler, Erich
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