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THE SAFE PREPARATION OF HTP AND CONCENTRATED H_2O_2 SAMPLES

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Abstract

The paper discusses the preparation of laboratory amounts of concentrated hydrogen peroxide solutions suitable for propulsion purposes (both types: stabilized and HTP class). A brief introduction to the physical properties, safety prescriptions, applications and material compatibility of hydrogen peroxide of HTP class is also presented for the sake of completeness. The final fragment concludes with a practical approach to the safe laboratory preparation method, handling and determination of purity and concentration of obtained concentrated hydrogen peroxide solutions.

INTRODUCTION

The paper summarizes the Space Technology Department at the Institute of Aviation goals for small spacecraft propulsion technology and link them to areas of propulsion research in Poland in general at the nearest future. A brief review of currently being investigated issue in the newly opened laboratory is presented as current and near term research, focused specifically on: concentrated solutions of H_2O_2 (stabilized and HTP - High Test Peroxide class) preparation, its long term storage possibilities, catalytic decomposition, "drop tests" for fuel ignition investigation, its use as "green" monopropellant or in hybrid rocket motors as the oxidant. By employing catalytic decomposition of HTP, auto-ignition of the solid fuel in a hybrid rocket is possible. When HTP is properly decomposed, the decomposition products alone release enough heat and the gases have suitable temperature (even over 700°C, depending on the concentration of the solution of peroxide) to provide efficient thrust.

Thus, at our new Laboratory of Propellants, unstabilized (HTP) as well as stabilized solutions of hydrogen peroxide from 75% up to over 90% concentration has been prepared in laboratory quantities for first investigations, that is: testing material compatibility and quasi-hypergolic ignition with potential fuels as well as long term storage on a small scale.

1. HYDROGEN PEROXIDE APPLICATIONS

The chemical compound named later as hydrogen peroxide was discovered by Thenard in 1818 and has been manufactured commercially by a variety of processes since about 1885. Today it is a versatile chemical, with numerous applications and it is routinely transported and stored in bulk quantities. In 1994 the worldwide production capacity for hydrogen peroxide was around 1.9 million tones and increased to 2.2 million in 2006 [1]. Nearly at the same time (1995) the first production line of industrial grades of H_2O_2 was started up in Poland (Pulawy) [2]. The most important current uses of lower grade H_2O_2 solutions include paper pulp and textiles bleaching, chemical synthesis, environmental treatment (waste water purification) and metals processing. These applications utilize hydrogen peroxide products which are generally considered as “standard” or “industrial grades”. These solutions of H_2O_2 are routinely shipped and stored worldwide, at maximum concentration 70%. The most commonly-used concentration in the world, however, is 50%, with customers diluting the 70% material prior to on-site storage [3].

There are also several specialty applications which demand either specially formulated stabilizer packages, for example cosmetic grades for consumer products, or very high levels of product purity (but not concentration) as required by the semiconductor industry. For the latter, hydrogen peroxide is typically supplied at a 30% concentration level (USLI grade - all metallic impurities are limited to a maximum of 10 ppb). The latter one was used by the authors as one of the raw solutions of H_2O_2 for HTP preparing.

There is a distinct growth in interest in the use of highly concentrated H_2O_2 (HTP) for propulsion applications that, perhaps, holds the promise of significant future demand [4]. Pure (or stabilised by other additives than phosphates) and highly concentrated hydrogen peroxide is a powerful oxidizing agent and efficient, environmentally friendly monopropellant (for small rocket engines used as attitude systems on satellites) as well, which is relatively easy to handle. Despite its power when concentrated, H_2O_2 is a natural metabolite of many organisms and has none of the problems of gaseous release or chemical residues that are associated with other chemical oxidants or rocket propellants. After its energetic decomposition, it is converted into plain ordinary water and oxygen. As an environmentally friendly and powerful rocket medium HTP has a long history of application to aerospace propulsion and power systems due to its high density, its monopropellant characteristics, its low toxicity and the ease of handling.

The use of high strength hydrogen peroxide as a rocket propellant can be traced back to Helmuth Walter and developments in Germany during the 1930’s. [5]. At that time, 80% hydrogen peroxide was first produced on a limited scale to support these developments. HTP is still produced in Germany today. Solvay Interox and Evonik (former Degussa) have their HTP producing facilities there and one of this sites has produced up to 87,5% H_2O_2 for many years, primarily for use in the propulsion systems (aerospace and defence related companies) or for manufacture of special organic chemicals. Today, HTP as a product, is still available in Europe to qualified end users only and can be imported into the US on an as-needed basis.

However, during the period of late 1980’s until recently, the demand for HTP had been, in practice, very small, which explains the current absence of commercial HTP production in the USA. Historically, USA demand had been more significant, and both Shell Chemical Company and FMC Corporation were producers of 90% H_2O_2, the latter company also producing some 98% H_2O_2 for a period of time. Shell’s hydrogen peroxide business was ultimately acquired by Interox and FMC ceased its production of HTP in the early to mid 1980’s. Recently, to meet the propulsion industry’s growing need for storable, low toxicity oxidizers, FMC has a production unit at its Bayport, that is capable of producing high-strength (70% to 98%) hydrogen peroxide. This high-test hydrogen peroxide is one of the highest purity product available in today’s market, meeting the most stringent specifications for monopropellant, bipropellant, and hybrid propulsion applications. However, FMC HTP hydrogen peroxide, similarly as the one from Evonik or other large companies, is available only to the selected end users, and is sold in specially designed and approved, large and costly containers, such as 30 gallon, high-purity aluminium drums or 4000 gallon high-purity aluminium tank trucks.

Unfortunately, none of the large suppliers of HTP does not include small containers of propellant grade HTP (or the price for them is extremely high; in the range of several hundred euro for one litre). Large drums are sold, but both availability and impurities have been variable. Also, handling larger quantities than needed can be very costly and burdensome in a small laboratory.

2. IMPORTANT FEATURES OF H_2O_2 SOLUTIONS

With the recent resurgence in interest in HTP amongst the aerospace community for propulsion applications, also our research team has focused some of its development efforts in this area. We have developed the laboratory methodology to safely and economically produce up to 99% H_2O_2 in laboratory quantities. We are currently completing hazard evaluation work on 90 - 99% H_2O_2, the results of which will enable us to analyze the safety risks associated with further preparation, transporting, storing and using products of various concentrations and purity in this range. This, in turn, will enable us to define the appropriate risk management measures required for an acceptably safe laboratory operating and future engine testing.

We have the knowledge that anyone conducting research and development work or using potentially hazardous materials should be completely familiar with its properties and behaviour and fully aware of appropriate handling, storage and disposal procedures, as well as necessary personal protective equipment. Hydrogen peroxide producers and suppliers have various safety materials available. The appropriate literature is also readily available in the internet. In fact, solutions of hydrogen peroxide always exhibit a minimal degree of instability, regardless of the concentration, continuously decomposing to water and oxygen with the evolution of heat;

H_2O_2 (l) H_2O (l) + ½O_2 (g) H = -98.4 kJ/mole
H_2O_2 (l) H_2O (g) + ½O_2 (g) H = -54.4 kJ/mole

It is well known now, that several factors affect the rate of decomposition, including temperature, degree of contamination, surface activity, pH, and to a lesser extent concentration. For example, the decomposition rate increases approximately 2,3 times for each 10°C rise in temperature. However, the normal rate of decomposition for commercial grades of hydrogen peroxide stored in compatible equipment is extremely low, typically much less than 1% loss (relative) per year.

It has been reported a decade ago that 90% peroxide stored for 17 years at ambient conditions in Texas showed a degradation in concentration of just 0.4% [6]. Furthermore, some other research have revealed that 98% hydrogen peroxide stored in 2.5 litre nitric acid bottles actually increased its concentration, to 99.5%, over a six month storage. That means, the rate of evaporation was greater than that of decomposition [7].

Pure concentrated hydrogen peroxide is really quite stable. In fact, concentrated H_2O_2 is generally more stable than a dilute solution (when uncontaminated). However, the particular resistance of any grade or concentration of H_2O_2 towards contamination is very dependent on the level (and type) of stabilizers used. Industrial grades of H_2O_2 (e.g. from Evonik, Arkema or Solvay Interox, 70% Technical and Chemical grades) are stabilized with various additives in order to provide a certain level of protection against the typical (low) levels of contaminants that may be experienced during transportation and storage in standard (passivated 304 or 316 stainless steel) equipment.

This stabilization, however, is not able to protect against "gross" contamination (which may mean levels below 1 ppm for certain contaminants, for example, Fe, Cu, Cr, or Mn ions, particularly in combination with each other) and in such instances slow decomposition of the product will commence.

In contrast, very lightly stabilized H_2O_2, such as that required by aerospace applications, is much more sensitive to contamination than the industrial grades due to the very limited amount of additives present. In order to ensure adequate stability for transportation and on-site storage, the choice of acceptable materials may be more restrictive and the use of standard" equipment may be in some circumstances inappropriate.

In addition to the homogeneous decomposition effects described above, there is also heterogeneous decomposition of hydrogen peroxide that occurs on some material surfaces. The magnitude of this effect can be quite large depending on the particular material and the surface condition. It is for this reason that relatively only a few materials are suitable for long term contact with H_2O_2 and careful attention must be paid to the preparation and conditioning of these surfaces during any tests.

For example, silver is one of the most active, which is actually a useful property exploited by the developers of decomposition catalyst systems for HTP/propulsion systems (Figure 1).

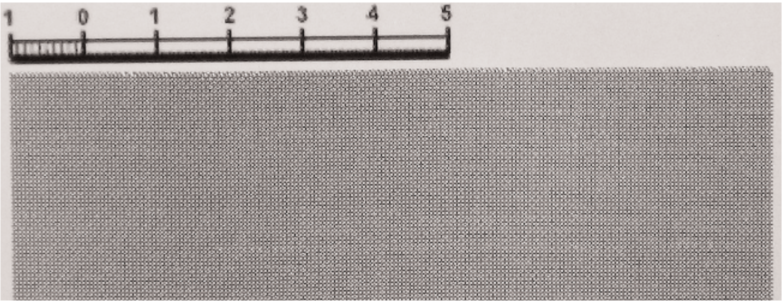


Fig. 1. Example of pure solid silver wire catalyst screen of 20 x 20 mesh (to be cut and pre-activated) (authors)

In contrast, certain grades of polyethylene and PTFE are completely inert towards HTP, thus are very suitable as material for containers (Figure 2).

Fig. 2. Row solutions (low concentration), samples of HTP (87,6%) and concentrated (stabilized, 86%) H_2O_2 prepared with the use of special vacuum rotary evaporator by the authors

For any given material, smooth surfaces are always less active than rough ones. Hydrogen peroxide compatible metal surfaces always require passivation and conditioning prior to use.

Thus, when considering materials compatibility, the effect of the peroxide on the material is generally much less important than the material's effect on the peroxide.

Since H_2O_2 decomposition is a significantly exothermic process (over 98 kJ/mole H_2O_2 at 25°C), the temperature of the decomposing solution will continue to rise if the generated heat cannot be effectively dissipated to the surroundings. This increase in temperature will increase the rate of decomposition resulting in a self-accelerating system. This generally applies to all concentrations of hydrogen peroxide. However, the magnitude of the consequences of H_2O_2 decomposition depends upon the initial concentration, and may be quite serious in the case of highly concentrated solutions.

Relatively large volumes of gaseous oxygen are evolved as hydrogen peroxide decomposes. If the peroxide strength is high enough, the material will boil and large volumes of steam will also be generated (Figure 3).

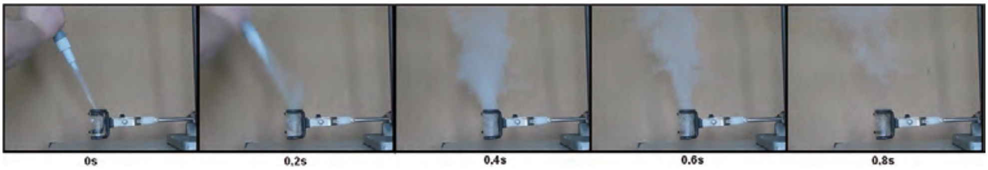


Fig. 3. Decomposition of 0,5 cm3 sample of 90% HTP
by one single crystal of KMnO4 (authors)

For concentrations up to 65% H_2O_2, the maximum adiabatic decomposition temperature that may be observed is 100°C; i.e. there is sufficient water present to absorb the total heat of decomposition by generation of steam. For concentrations above 65%, the final adiabatic temperature that may be attained increases with increase in initial H_2O_2 concentration. For solution of 70% H_2O_2, the heat of decomposition is 1,984 kJ/g solution and the adiabatic decomposition temperature is 233°C, with a volume expansion of 2500 times the starting volume. For 85% H_2O_2, the heat of decomposition is 2,453 kJ/g with a potential adiabatic temperature of 613°C and a volume expansion ratio of 4500.

3. COMPATIBILITY WITH THE STRUCTURAL MATERIALS AND SAFETY

The effects associated with materials in contact with hydrogen peroxide can vary widely, thus a standard method of classification according to likely performance in service has been devised as follows:

Class 1: Materials that are fully compatible with hydrogen peroxide and suitable for long term contact such as storage tanks.

Class 2: Materials that are satisfactory for repeated short term contact with hydrogen peroxide prior to storage or use. Contact time should be quite short prior to storage. Contact time should not exceed four hours at 71°C or one week at 21°C prior to use [8].

Class 3: Materials that are suitable for short term contact only, prior to prompt use.

Class 4: Materials that are unsuitable or hazardous for any use with hydrogen peroxide.

The requirement for class 1 materials for long term contact is not unique to concentrated H_2O_2 and in fact applies to all concentrations. However, a material that is rated class 1 for storage of 50% H_2O_2, for example, may not carry the same rating for storage of 70% or 85% H_2O_2.

For storage of high purity 70% H_2O_2 or 85% H_2O_2, class 1 materials are PTFE lined stainless steel (304L or 316L) or 99.5% aluminium. Other aluminium alloys may be used but the exact composition of the alloy can significantly impact the rate of metal pick-up and hence have an effect on the product stability and purity.

Hydrogen peroxide is non flammable substance. However, it can form explosive vapours under certain conditions (explosion occurring by decomposition of the vapour rather than combustion). This potential hazard is a function of temperature, pressure, and H_2O_2 liquid concentration. At the ambient pressure, boiling 74% hydrogen peroxide (at 130°C) will give a vapour just at the limit of flammability. This is a kind of lower explosive limit for H_2O_2 vapour and its value is 26 mole % (39 wt. %) at atmospheric pressure. For liquid concentrations higher than 74%, explosive vapours can be generated at temperatures less than their normal boiling points (Fig. 4).

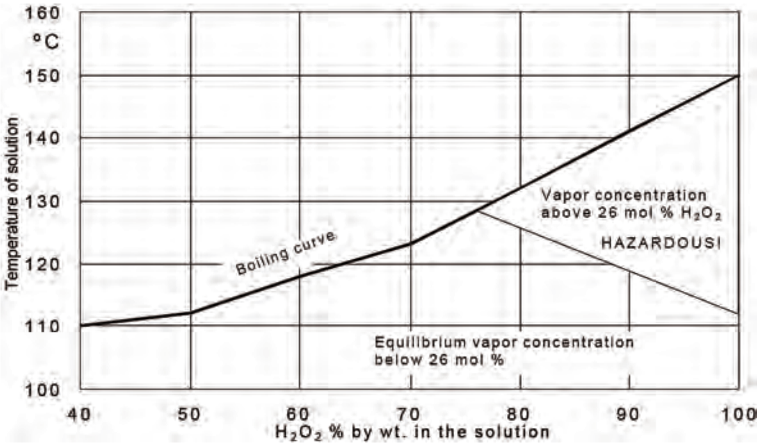
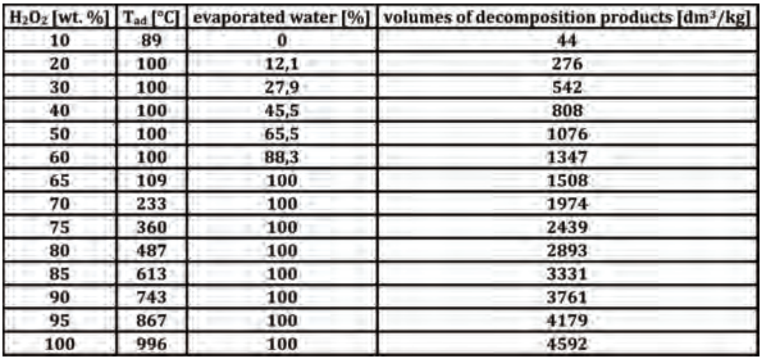


Fig. 4. Phase Diagram Showing the Explosive Range of Hydrogen Peroxide [9]
For example, for 85% solution of H2O2 at atmospheric pressure, a temperature of 121°C is required to generate an explosive atmosphere (a boiling point of the solution is equal 139°C).

As the pressure increases, flammable atmospheres are achieved at progressively lower concentrations of boiling liquid, until a pressure of 4 bar is reached. At this pressure, the limit of flammability of H2O2 vapour is 33 wt. %, which is in equilibrium with boiling 66.5% H2O2. Above 4 bar, the flammable limit of the vapour remains constant at 33 wt. % and the equilibrium liquid concentration falls very slowly as pressure increases.

Tab. 1. Calculated adiabatic temperature of decomposition products and their volume for solutions of H2O2 [10]



H_2O_2 [wt. %]	T_{ad} [°C]	evaporated water [%]	volumes of decomposition products [dm^3/kg]
10	89	0	44
20	100	12,1	276
30	100	27,9	542
40	100	45,5	808
50	100	65,5	1076
60	100	88,3	1347
65	109	100	1508
70	233	100	1974
75	360	100	2439
80	487	100	2893
85	613	100	3331
90	743	100	3761
95	867	100	4179
100	996	100	4592

Decomposition of hydrogen peroxide solutions can, of course, raise their temperature to boiling point and evaporate water and hydrogen peroxide (Table 1). In the absence of any other

The large volumes of oxygen generated as H_2O_2 decomposes further add to this potential problem. Oxygen enrichment atmospheres greatly increase the fire hazards posed by flammable liquids, vapours and gases. First of all, oxygen enrichment widens the explosive limits. It does not affect the flash point significantly, so materials below the flash point remain safe. The increase is into the fuel rich area. It also greatly reduces the energy required to produce ignition and increases the rate.

Even dilute hydrogen peroxide can create potential problems. For example 3% H_2O_2 generates 10 volumes of oxygen for each volume of H_2O_2 decomposed. Oxygen enrichment of confined spaces is therefore a real possibility. Dilution with copious amounts of water is the appropriate response to spillage of hydrogen peroxide. Entrapment in confined spaces must be actively avoided.

3. CURRENT DEVELOPMENTS – PREPARATION OF HTP IN THE LABORATORY

Chemically pure (pure for analysis) and electronic grade (ULSI class) 30% hydrogen peroxide was purchased in 5 liter polyethylene containers. It was then concentrated up to 92% by using the apparatus shown in Figure 5. Some of the obtained solutions of concentrated H_2O_2 meet the requirements for HTP class (those prepared from ULSI solutions). Operation is mainly automated, so only daily emptying and filling of vessels is required to yield about 2 liters of HTP over a regular work week. The cost per liter is high, but still acceptable and affordable.

Fig. 5. The equipment for safe, evaporative concentration (by vacuum distillation) of H_2O_2 low concentration solutions (authors)

This laboratory method of HTP (H_2O_2) preparation simplifies the apparatus at the maximum level and reduces glassware cleaning. The method in fact consists of two crucial steps: a) the phase of low temperature concentration of hydrogen peroxide via forced evaporation under fume cupboard (can be omitted), b) further concentration and purification via distillation under reduced pressure with use a special rotary vacuum evaporator Nahita model 503.

The whole setup used in the preparation consisting of an off-the-shelf borosilicate glass rotary vacuum evaporator and a special vacuum system. The solution concentrated to about 85 - 90% and having several dozen ppm concentrated impurities will be heated in 1 dm3 batch by a water bath at 55°C. The solutions of ultra-high purity strait after the process of evaporation (concentration) held the requirements for HTP class (prepared from ULSI solutions of H_2O_2). The sealed glassware was hold internally below 40 milibar, which enabled rapid evaporation over a period of 2,5 - 3 hours. Condensate dripped into the collector flask with no more than a few percents loss. The circulation of cold water through a chiller, at the condenser coils, enabled condensation with minimum losses. Vapors of hydrogen peroxide which escaped the condenser were rendered harmless by dilution in the laboratory fume hood. Prepared HTP is stored in a special containers with a vent ports, since gradual decay to oxygen and water might cause pressure buildup and the rapture of the vessel. However, the situation even with the slightest overpressure in the HTP or concentrated and stabilized H_2O_2 container was never experienced so far during the routine experiments by the authors.

Several distillation processes were carried out in total allowing to obtain a few samples of stabilized concentrated H_2O_2 and HTP. The concentration was determined with great accuracy (up to second digit after dot) by utilizing a special high precision aerometer and use the Evonik model to calculate the concentration from the corresponding density of hydrogen peroxide (Figure 6) [11].

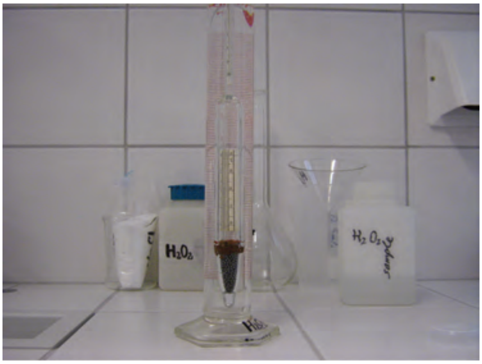


Fig. 6. High precision aerometer used to determine the density
of HTP/H2O2 solutions (authors)

An electronic conductivity meter was used to test the purity of obtained solutions of HTP and concentrated H_2O_2. In the case of HTP the value of conductivity was virtually close to 0 μS/cm, whereas for stabilized solutions of concentrated H_2O_2 was in the range of several hundreds of μS/cm. Test for phosphate measurement for water quality testing was also applied to the HTP solutions as a quick, easy, and reliable test for measuring phosphates in them, with 200 ppb as the lowest detection level. The results were negative what confirmed the conductivity measurements (the level of phosphates was in the range appropriate for HTP class, that is below 0,2 ppm). The level of pH was also trialed, showing the acidity that is more suitable for concentrated H_2O_2/HTP solutions (lowering the rate of decomposition) (Figure 7).

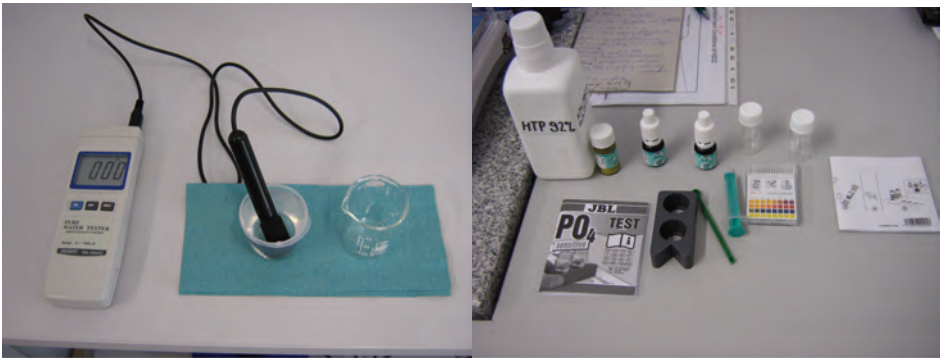


Fig. 7. The conductivity of HTP solutions was in the same range as those
for deionized water whereas the level of phosphates under 200 ppb (authors)

CONCLUSIONS

Hydrogen peroxide is a safe and versatile chemical, monopropellant and oxidizer if handled and stored properly. With the correct materials of construction, properly prepared in the laboratory and conditioned, the chemical is very storable, normally decomposing at extremely low rates.

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BEZPIECZNA METODA PREPARATYKI HTP ORAZ STĘŻONYCH ROZTWORÓW NADTLENKU WODORU

Streszczenie

W artykule przedstawiono prosty sposób preparatyki laboratoryjnych ilości stężonego nadtlenku wodoru dla celów napędowych (zarówno stabilizowanego, jak i czystego, klasy HTP). Omówiono również podstawowe właściwości fizyczne tej substancji, wraz z uwzględnieniem wymogów związanych z jej bezpiecznym użytkowaniem podczas badań oraz w technicznych aplikacjach. Zwrócono uwagę na takie aspekty jak kompatybilność materiałowa oraz stabilność. Przedstawiono również prosty i skuteczny sposób określania czystości oraz stężenia uzyskiwanych w laboratoryjnych warunkach stężonych roztworów nadtlenku wodoru.