High-Purity Fixed Points of the ITS-90 with Traceable Analysis of Impurity Contents

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Abstract   The International Temperature Scale of 1990 (ITS-90) is based on thermodynamic equilibrium states of ideally pure substances. The largest contribution to the uncertainty budgets of most metallic fixed points is the influence of impurities on the fixed-point temperature. Therefore, a traceable chemical analysis of the remaining impurities with small uncertainty is the basis of further progress. Further requirements are better knowledge of the phase diagrams at very low impurity contents, impurity segregation, and the quantification and correction of thermal effects during a fixed-point realization. In this article, current and future activities at PTB and BAM in order to develop improved metallic fixed-point cells of the ITS-90 are reviewed.

1 Introduction

The fixed-point temperatures of the International Temperature Scale of 1990 (ITS-90) are defined by first-order phase transitions of ideally pure substances. Therefore, there is a consensus within the temperature community that more extensive proofs of the purity of fixed-point materials are essential in order to achieve further improvements [1]. If the content of impurities in the fixed-point material and their specific influences are known with sufficiently small uncertainty, a correction of the fixed-point temperature could be applied (SIE-method, sum of individual estimates).

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A further question is whether it is possible to demonstrate that a given cell is sufficiently uncontaminated for use as an ITS-90 fixed point. A non-destructive determination of the mean impurity content of a fixed-point cell after a specific period of operation is currently difficult to imagine because of the inhomogeneous distribution of impurities in the vertical and radial directions and their segregation within the crystal or at grain boundaries. Therefore, there is considerable interest in attempts [2–6] to derive complementary information from fixed-point measurements themselves. In recent years, it has been clearly demonstrated [1,7] that an approach based on Raoult's law is appropriate only for impurities that are insoluble in the solid fixed-point material, and there are further well-known problems, e.g., the diffusion of impurities in the melt and the resulting effective distribution coefficients which might be very different in comparison to their equilibrium values (partial mixing). Nevertheless, the utility information that can be extracted from a series of complementary fixed-point realizations (like freezing/melting with/without second interface, melting after slow/fast cooling, variations of the duration of the fixed-point plateau and subsequent extrapolation, adiabatic measurements and other techniques) is currently a matter of active discussion.

Therefore, at PTB, fixed-point cells were doped with impurities of different behavior in order to understand to what extent their specific influence depends on the method of fixed-point realization and to obtain more accurate data on their binary phase diagrams.

Furthermore, it is necessary to separate the influences of thermal and impurity effects on the shapes of the freezing and melting plateaux.

2 Sample and Crucible Preparation

Fixed-point materials like indium, tin, zinc, and aluminum are molten or frozen in graphite crucibles. The fixed-point cells manufactured at PTB are very similar to a well-established design developed by Bongiovanni and colleagues with minor modifications considering the recommendations described in [8]. The crucible and thermal insulation are enclosed within a closed-end quartz tube with a stainless steel cover and o-ring seal at the top to allow evacuation and operation in a high-purity argon atmosphere at a known pressure. A carbon-fiber-based material with low ash content ($<20\,\mu g \cdot g^{-1}$) is used as thermal insulation above the graphite crucible. The pressure in the fixed-point cell is measured by means of a Setra Model B370 pressure gauge.

Initially, several surface-cleaning steps are carried out in order to avoid contamination of the fixed-point material by other parts of the cell. All quartz and stainless steel parts are cleaned in a laboratory glassware dishwasher and subsequently purged with distilled water.

The crucibles, consisting of an isostatically-pressed fine-grain graphite (Type 7710, SGL-Carbon, Bonn), are manufactured according to PTB specifications. After fabrication of the crucibles and other graphite parts, a proprietary cleaning procedure is used by the manufacturer in order to ensure the specified purity levels (ash content $<5\,\mu g \cdot g^{-1}$). Table 1 shows the results of a GD-MS analysis of the delivered graphite carried out by an external service provider (Aqura GmbH).

Table 1 Results of GD-MS analysis of the high-purity graphite used for fixed-point crucibles

Element	Mass fraction (ng · g^{-1})	Element	Mass fraction (ng · g^{-1})
Ag	<42	Mo	<31
Al	<10	Na	≤100
As	78	Nd	<10
Au	<29	Ni	<32
B	<11	Os	<24*
Ba	<5	P	<14
Bi	<14	Pb	<16
Br	<120*	Pd	<18*
Ca	<160	Pr	<3
Cd	<62	Pt	<13*
Ce	<3	Rb	<6*
Co	<7	Re	<5*
Cr	<240	Rh	<5*
Cs	<4*	Ru	<10*
Cu	<34	S	≤ 300
Dy	<13	Sb	<45
Er	<9	Sc	<2
Eu	<7	Se	<210
Fe	19	Si	310
Ga	<61	Sm	<12
Gd	<10	Sn	<100
Ge	<390	Sr	<10
Hf	<14	Tb	<3
Hg	<110	Te	<77
Ho	<4	Th	<2
I	<3*	Ti	<7
In	<18	Tl	<7*
Ir	<11*	Tm	<4
La	<3	U	<2
Li	<8	V	<4
Lu	<4	Y	<3
K	<310	Yb	<19
Mg	<150	Zn	<41
Mn	<10	Zr	<7

The laboratory has stated that most of the analysis results are expected to be within a factor of two of the values obtained. If there was no standard RSF (see Fig. 1) available (designated by "*"), a factor of five was stated

Before filling the crucible with the fixed-point material, all parts are assembled and baked out for more than 24 h under vacuum at least 300 K above the fixed-point temperature. The filling of the crucibles with fixed-point materials is carried out in a glove box within an argon atmosphere. For the other preparation steps, a laminar-flow box is used. After filling the crucible with the high-purity metal, the cell is heated to a

temperature close (depending on the vapor pressure) to the melting temperature of the metal and permanently evacuated in order to remove remaining gaseous impurities. The pressure during this treatment is kept below 0.01 Pa for several hours (except for zinc because of its high vapor pressure).

3 Chemical Analysis of High-Purity Materials

3.1 Glow Discharge Mass Spectrometry

The current state-of-the-art approach for the determination of the impurity content of fixed-point materials is based on glow discharge mass spectrometry (GD-MS). Advantages of this technique are low limits of determination, excellent repeatability, and a direct solid sampling technique that avoids losses or contamination caused by wet chemical pretreatment. In contrast to most other techniques, it is considerably faster and results can be obtained within minutes to a few hours. Typically, a large number of about 50–70 different impurities (elements of the periodic table) can be determined with sufficiently low limits of detection down to the $ng \cdot g^{-1}$ level. Some manufacturers of high-purity materials and specialized laboratories operate this type of instrument and provide customers with the results of their analysis. An example of an analyses according to the state-of-the-art can be found in [1].

Nevertheless, the main drawback of this method is the lack of a suitable and traceable calibration procedure for the quantification of low mass fractions with small uncertainty. With the current method of quantification for GD-MS, which is based on matrix-independent analyte-specific so-called standard relative sensitivity factors (Standard-RSF), uncertainties between a factor of two (of the true value) and a factor of five are typically claimed. Given this context, CCT-WG1 agreed that a fixed-point temperature should not be corrected when the uncertainties of the chemical analysis exceed 100%. This is because the application of the correction in this case may do more harm than good. Further problems include insufficient knowledge of the homogeneity of a specific batch of fixed-point material and the reproducibility of the chemical analysis by other laboratories.

PTB ordered a specific batch of fixed-point material, and samples were sent for chemical analysis to different laboratories in order to check the reliability of the results. Table 2 shows some results of such a comparison for an indium sample declared to have 7N purity. It is clearly shown that the results considerably disagree for some impurities, in two cases by more than two orders of magnitude. Similar results were also found when the results of different laboratories for high-purity zinc were compared. In most cases, the same type of GD-MS instrument was used. Comparing the results of one laboratory for the same batch of material indicated that this seems to be neither a problem with the homogeneity of a specific batch of material nor a problem with the repeatability of measurements carried out at a specific laboratory. This is a topic of further investigations.

As a consequence, the use of the SIE-method to correct for the influence of specific impurities is considered inappropriate if based on the analysis of only one laboratory.

Table 2 Comparison of results of GD-MS analysis on two samples of the same batch of high-purity indium declared to have 7N purity

Element	Amount fraction Laboratory 1 (ppb_{molar})	Amount fraction Laboratory 2 (ppb_{molar})
Ag	426	<1
S	358	<5
Cu	72	6
Pb	55	42
Cr	44	<1
Ga	16	<1
Bi	11	6
Se	4	<5
Sb	3	2
Tl	<1	5

Measurements were carried out by two different laboratories with the same type of GD-MS instrument (VG-9000). Laboratory 1 has stated a factor of two as the uncertainty for the concentrations of the elements shown here. Laboratory 2 has not stated an uncertainty within the certificate. After a request, it was stated that the analysis results are expected to be within a factor of two of the values obtained. For all other impurities, the results agree. This is because at least one of the laboratories has given a sufficiently high detection limit

In close cooperation with PTB, BAM is therefore developing a methodology for certifying the purity of ultra-high purity fixed-point materials. For this investigation, a GD-MS instrument type ELEMENT GD (manufacturer: Thermo Fisher Scientific Inc.) is used. The basic principle of the new methodology for the instrument calibration is to replace the current semi-quantitative approach by a quantitative one based on sets of doped samples with well-known impurity content whose values are directly traceable to the International System of Units (SI) and that provides measurement results with small uncertainty down to the $ng \cdot g^{-1}$ level (Fig. 1) [9]. Such a methodology is the most accurate procedure to obtain small uncertainties using GD-MS. To date, calibration sets of high-purity zinc doped with eight different impurity fractions between $5\,ng \cdot g^{-1}$ and $10\,\mu g \cdot g^{-1}$ have been established. Each set consists of the high-purity matrix material and 52 elements of the periodic table, doped as liquid standard solutions into the matrix powder under clean conditions, then dried, mixed, and pressed under $90\,kN \cdot cm^{-2}$. Similar work for other high-purity materials is in progress.

This calibration is checked by GD-MS measurements on existing certified reference materials with well-known impurity contents. Figure 2 shows the results of an instrument calibration for high-purity zinc samples doped with well-known amounts of cadmium (measured for isotope ^{112}Cd). It can be seen that the results of measurements on four different certified reference materials are in very good agreement with respect to their certified cadmium content.

These investigations are accompanied by intercomparisons with the GD-MS results of other research institutes both for the same sample and for samples of the same batch of material. In the next stage, a new way of determining non-metallic trace elements with small uncertainty by GD-MS will be investigated.
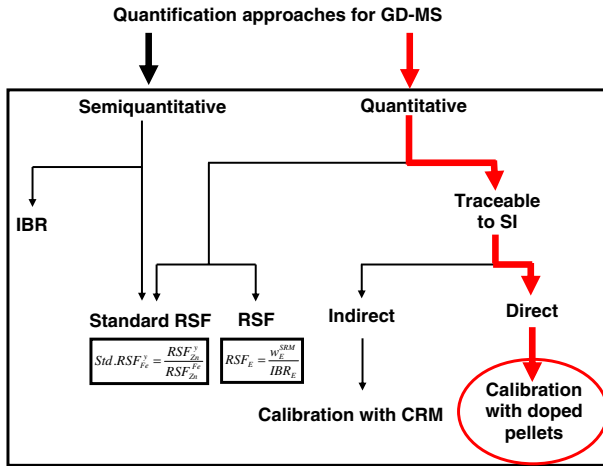
Fig. 1 Possible approaches for quantification by GD-MS (glow discharge-mMass spectrometry) analysis. Matrix-normalized analyte signals (IBR) are plotted against the known concentrations. Stars and the straight line represent the calibration using doped zinc pellets. Dots represent measurement results of certified reference materials; IBR—ion beam ratio, RSF—relative sensitivity factor
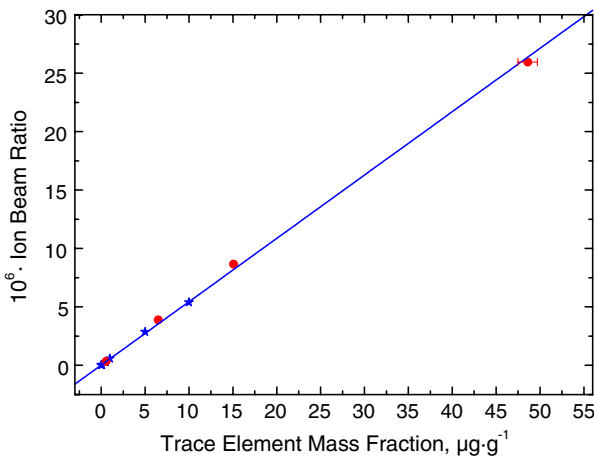

Fig. 2 Calibration curve of cadmium in a zinc matrix (for isotope ^{112}Cd, medium resolution) Measurements were carried out with the GD-MS instrument "Element GD;" stars—calibration, dots—certified reference materials

3.2 Complementary Methods

A disadvantage of GD-MS is that it is difficult to quantify with small uncertainty, especially for non-metals. Complementary methods for metal determination are inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), and instrumental neutron activation analysis (INAA) techniques. The determination of the carbon content and that of dissolved gases such as oxygen and nitrogen is a significant problem. For the determination of non-metals, carrier gas hot extraction

(CGHE) and photon activation analysis (PAA) are suitable complementary methods. BAM has determined the content of oxygen, nitrogen, carbon, and sulfur in a high-purity indium fixed-point material from PTB by means of carrier gas hot extraction. The results are: $w(O, In) < 2.0\,\mu g \cdot g^{-1}$, $w(N, In) < 3.7\,\mu g \cdot g^{-1}$, $w(C, In) < 10\,\mu g \cdot g^{-1}$, and $w(S, In) < 11\,\mu g \cdot g^{-1}$, based on the limit of determination (6s criteria). It can be seen that the detection limits of the current generation of instruments for carrier gas hot extraction are not low enough to fulfill the requirements of thermometrists. Further investigations by other techniques are underway.

Besides the problem with too high limits of detection, other investigations at BAM have shown that dissolved gases are often the impurities with the highest content within high-purity metals. On the other hand, there is good reason to believe that a considerable portion is extracted by evacuation of the fixed-point cell at high temperatures, although there is currently no established method to determine the remaining content of dissolved gases in a fixed-point cell. As a consequence, the study and comparison of fixed-point cells after different evacuation procedures at temperatures close to the melting point and operated with different inert gases is considered the method of choice to study the influence of dissolved gases.

Summarizing, a considerable effort is required in order to quantify the impurity content in materials used for ITS-90 fixed points. This includes careful investigations by different methods and proof of the homogeneity of each specific batch of a material. This advises the investigation and certification of larger batches of materials which would be made available to all NMIs, as suggested in [10].

4 Phase Diagrams

The specific influences of different impurities can be derived either directly from binary phase diagrams [11] or by means of so-called CALPHAD-methods [12–14], i.e., software for the calculation of phase diagrams (e.g., MTDATA, FactSage, Thermo-Calc). Further sources of information include doping experiments on fixed-point cells or investigations by adiabatic calorimetry [15–17].

At PTB, literature data on binary phase diagrams at low impurity content were collected and compared, including the slopes of liquidus and solidus lines and equilibrium distribution coefficients. It was found that there are a considerable number of binary systems where the data from different sources are significantly discrepant. The worst cases are the so-called "0% systems" [14] where even the sign of the slope of the liquidus line (temperature decrease or increase) might be unknown.

The main reason for the disagreement is that most of the underlying experimental data used for textbooks on binary phase diagrams were determined at impurity concentrations several orders of magnitude larger than that within ITS-90 fixed-point materials. Although phase diagrams calculated by the CALPHAD-methods appear more reliable, they are also limited by the lack of data at very low concentrations. Therefore, the experimental investigation of phase diagrams at very low impurity content seems necessary when correction of the fixed-point temperature according to the SIE-method is intended. At PTB, currently three experimental setups are used for these investigations.

The first one which was recently completed is an adiabatic fixed-point calorimeter for temperatures between 20°C and 450°C and a sample mass between 100 g and 150 g. The main applications will be the screening of larger portions of binary phase diagrams of indium, tin, and zinc with impurity concentrations between about $5\,\mu g \cdot g^{-1}$ and $100\,\mu g \cdot g^{-1}$ and the investigation of alternative crucible materials. Therefore, this instrument was optimized for quick and easy operation and sample changes. A typical uncertainty of about 0.5 mK is achieved.

The second setup was developed to compare fixed-point materials from different sources, to carry out doping experiments at very low concentrations, ($<5\,\mu g \cdot g^{-1}$), and to study forced ageing of fixed-point cells. This requires the lowest possible uncertainties on a level of 0.2 mK or better. It is based on slim fixed-point cells with a sample mass of about 250 g [18].

The third approach is associated with fixed-point cells of standard design. One type of investigation is associated with older cells that were operated for more than 10 years, and that are preferably slightly contaminated. These investigations were started to study the influence of impurities that might increase the freezing point and to gain a better understanding of whether different methods of fixed-point realization can be used to identify specific types of impurities. As an example, a contaminated tin cell with an initial fixed-point temperature about 2.7 mK below the national standard was doped with small amounts of antimony [19]. It is well known that doping of tin by antimony will result in a higher fixed-point temperature and it was observed [15] that doping could improve the flatness of the plateau. Similar measurements were carried out by doping a zinc cell with silver.

A further matter of interest is to study the influence of mutual interactions of different types of impurities within a thermometric fixed point. This can be investigated by doping experiments on cells of different initial purity (e.g., 7N, 6N, 5N5). If mutual interactions between different types of impurities are negligible in all cases, the same slope of the liquidus line is expected. More details and first results on this topic are found in [19,20].

5 Thermal Effects

In recent years, many NMIs have modified the design of their fixed-point cells in order to allow their operation in an inert gas atmosphere at a well-known pressure. These improvements are often associated with increased heat losses. It is well known (e.g., [21]) that very good results can be achieved by using the maximum of the freezing curve as the liquidus temperature, even if a less-advanced fixed-point furnace is used. This is because of the very low dependence of this maximum temperature on the homogeneity and stability of the furnace temperature. On the other hand, the slopes of freezing and melting curves depend on both the homogeneity of the temperature profile of the furnace and the segregation of impurities [18]. In order to derive complementary information on the segregation of impurities during a fixed-point realization, better understanding and the correction of thermal effects are necessary.

As an example, Fig. 3 shows the melting curves of an indium fixed-point cell with three different immersions of the standard platinum resistance thermometer (SPRT).
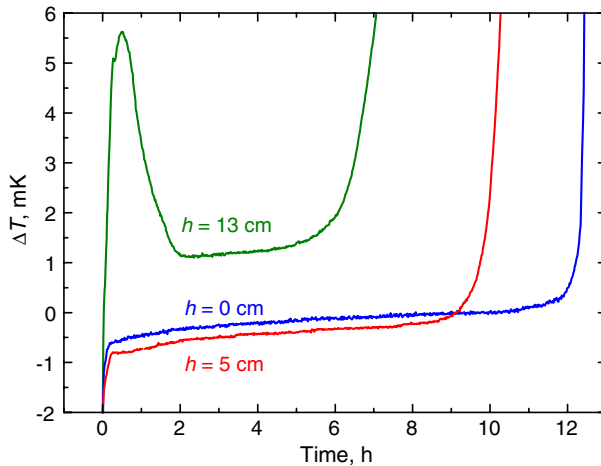
Fig. 3 Melting of an indium fixed point in a water heat-pipe furnace at different immersions

The measurements were carried out in a water heat-pipe furnace at a temperature difference between the furnace and fixed-point temperature of about 1 K. The measurements at full immersion (0 cm) and at 5 cm above the bottom of the cell show the expected plateau temperatures according to the hydrostatic pressure gradient. Furthermore, it can be seen that the duration of the plateau changes considerably with immersion depth, indicating that melting finished first at the top of the cell. However, the measurement results at 13 cm above the bottom of the cell are not in agreement with the common understanding of immersion behavior. According to our understanding, at the beginning of the melt, the overheated liquid is partly extruded to the top of the cell (because of the volume change on melting) and forms an overheated liquid thermal bridge causing a higher temperature in the upper part of the fixed-point cell; the overheated liquid forces melting at the top of the cell. Therefore, the peak disappears after some time. It should be noted that with three-zone fixed-point furnaces, overheating of more than 20 mK is easily achieved. This shows that the proper determination of the influence of thermal effects on melting by the measurement of immersion characteristics requires detailed investigations and the consideration of transient effects.

Recent investigations at PTB have shown that for specific fixed-point cell/furnace combinations, other parts of the freezing curve, and therefore its slope, are considerably influenced by the temperature profile of the furnace [18]. This was demonstrated by using a sequence of stepwise changes of the furnace temperature during a fixed-point realization. Therefore, the determination of an impurity-dependent relationship between the plateau slope as a function of the melt-fraction (1/F-characteristics) is questionable if this is not properly considered. Otherwise, a sloping freezing curve which is caused by a thermal effect might be misleadingly attributed to the influence of impurities.

As a consequence, at PTB, a new method was developed that allows study of different fixed-point cells (cell designs) with respect to their sensitivity to changes of the furnace temperature. This method is based on the measurement of the freezing

temperature of a fixed point while the furnace temperature is changed. The result is a damping ratio for temperature changes, μ, as a function of the melt-fraction and immersion which characterizes the thermal coupling between the measured fixed-point temperature and the furnace temperature. First results of these investigations have led to improvements in the current fixed-point design. These include changes to the distance between the graphite thermowell and the bottom of the crucible and in the thermal contact between the thermowell and graphite crucible above the fixed-point metal in the upper part of the cell. More details can be found in [17]. A further activity is the investigation of different sand-blasting techniques for the quartz parts of a cell in order to further reduce heat losses by thermal radiation ("light-piping") at the zinc, aluminum, and silver fixed points.

6 New Fixed-Point Cells

The final objective of these investigations is to produce a new generation of fixed-point cells that allow the realization and dissemination of the ITS with smaller uncertainties. As a first step, one zinc and two indium fixed-point cells were produced with materials of nominally 7N purity. These new cells were compared with other cells in order to study whether the differences of fixed-point temperatures are in agreement with the expected shift derived from the results of the chemical analysis. For this comparison, the usual procedures and equipment (fixed-point furnaces, SPRTs, and thermometry bridges) were used. In accordance with the BIPM key comparison database, the expanded ($k = 2$) uncertainties for the comparison of fixed-point cells at PTB amount to 0.85 mK for indium and 1.3 mK for zinc cells. The fixed-point temperatures are measured on a regular basis in order to check whether the cleaning procedures were sufficient. Furthermore, the new cells are investigated in different fixed-point furnaces to study the influence of thermal effects.

The freezing temperature of the new zinc cell is close to the national standard (0.4 mK below) and therefore is in very good agreement with other working standards used at PTB. A state-of-the-art GD-MS analysis of 57 investigated elements indicated that the sum of the remaining impurities is less than $200\,\text{ng} \cdot \text{g}^{-1}$ if the results for carbon and oxygen are excluded. Based on these results, a maximum shift of the fixed-point temperature of about $110\,\mu\text{K}$ is expected if the influences of carbon, as well as oxygen and other dissolved gases, are neglected. Measurements of two new indium fixed-point cells have confirmed that they are in very close agreement ($150\,\mu\text{K}$) with the national standard. Further investigations are in progress in order to achieve lower measurement uncertainties. Two GD-MS analyses of more than 50 investigated elements for one of the two batches of indium were carried out by two different laboratories. If the contents of carbon and dissolved gases are excluded, one laboratory confirmed the declaration of the manufacturer and determined a mass fraction of all investigated elements of about $0.1\,\mu\text{g} \cdot \text{g}^{-1}$, the other laboratory determined a mass fraction of about $0.7\,\mu\text{g} \cdot \text{g}^{-1}$. Next, independent and traceable chemical analysis of these substances by BAM as well as more accurate fixed-point comparisons on new slim fixed-point cells filled with material from the same batches are planned.

7 Conclusions

It has been shown that further progress in the development of fixed points requires the consideration of different aspects, i.e., SI traceable chemical analysis with smaller uncertainties, more experimental validation of liquidus slopes for fixed-point impurities, and the influence of static and transient thermal effects depending on the type of fixed-point realization.

Taking into account the current uncertainties of chemical analysis and liquidus slopes, the application of the OME-method (overall maximum estimate) for the estimation of the uncertainty contribution due to impurities is preferable to the SIE method. If the required effort for a traceable chemical analysis is considered, the use of larger certified batches of materials of the highest purities (reference materials) available to all thermometrists is considered the most reliable way to ensure the long-term stability of the scale and to approach the phase-transition temperature of the pure substance.

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