EUROPEAN COOPERATION

ECSS

FOR SPACE STANDARDIZATION

Space product assurance

Kinetic outgassing of materials for space

Foreword

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Change log

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Scope

This Technical Memorandum defines the state of the art test methods and related modelling for evaluating the long term outgassing characteristics of materials.

The methods that are currently used for temporal and temperature variant sources and collectors are the ESTEC test method, the CNES test method and the ASTM E1559 standard long term outgassing method. These allow accurate temporal profiling of the outgassing and in addition, with the aid of modelling software, in-orbit predictions of emissions, transport and depositions.

2
References

ECSS-ST-S-00-01	ECSS system - Glossary of terms
ECSS-Q-ST-70-02	Space product assurance - Thermal vacuum outgassing test for the screening of space materials
ASTM E1559-09	Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials
	"Progress on the Physical Approach to Molecular Contamination Modeling", Journal of Spacecraft and Rockets, 2011 vol. 48 no. 2 (Jean-François Roussel et al.)

3
Terms, definitions and abbreviated terms

3.1 Terms from other documents

For the purpose of this document, the terms and definitions from ECSS-S-ST-00-01 apply.

3.2 Terms specific to the present document

3.2.1 Collected Volatile Condensable Material (CVCM)

quantity of outgassed matter from a test specimen that condenses on a surface maintained at a specific constant temperature, as a function of the outgassing test time

> NOTE 1   CVCM is expressed as a percentage of the initial specimen mass.
>
> NOTE 2   This is not necessarily the same as the CVCM determined by ECSS-Q-ST-70-02.

3.2.2 Knudsen cell

container with a cylindrical orifice in which a material sample is placed and heated to the testing temperature(s)

> NOTE 1   The Knudsen cell has a cylindrical orifice from which the evolving gases exit in a controlled way. Sizes of the Knudsen cell, including the orifice, are specified to allow free molecular flow of the evolving gases and to allow predicting the molecular flux from the orifice.
>
> NOTE 2   Also known as Effusion cell

3.2.3 Quartz Crystal Microbalance (QCM) ThermoGravimetric Analysis (TGA)

technique in which a QCM is heated at a constant rate and the (remaining) deposited mass is recorded as a function of time and temperature

> NOTE   The aim is to determine the evaporation characteristics of the species in the deposit.

3.2.4 Recovered Mass Loss (RML)

total mass of material outgassed from a test specimen that is maintained at specified temperature(s) and operating pressure, as a function of the outgassing test time, without the absorbed water

> NOTE 1   RML is expressed as a percentage of the initial specimen mass.
>
> NOTE 2   This is not necessarily the same as the RML determined by ECSS-Q-ST-70-02.

3.2.5 Total Mass Loss (TML)

total mass of material outgassed from a test specimen that is maintained at specified temperature(s) and operating pressure, as a function of the outgassing test time

> NOTE 1   TML is expressed as a percentage of the initial specimen mass.
>
> NOTE 2   This is not necessarily the same as the TML determined by ECSS-Q-ST-70-02.

3.3   Abbreviated terms

For the purpose of this document, the abbreviated terms from ECSS-S-ST-00-01 and the following apply:

Abbreviation	Meaning
COMPEX	contamination model parameter extractor
CVCM	collected volatile condensable material
DOK	dynamic outgassing Knudsen cell
FTIR	Fourier transform infrared spectroscopy
GC/MS	gas chromatography / mass spectrometry
GN_2	gaseous nitrogen
IPA	isopropyl alcohol
MIC	materials identification card
MSE	mean squared error
QCM	quartz crystal microbalance
RGA	residual gas analyser
RH	relative humidity
RML	recovered mass loss
TGA	thermogravimetric analysis
TML	total mass loss
VBQC	vacuum balance quartz crystal
WVR	water vapour regained

4
The physics and its modelling

4.1 Outgassing

4.1.1 Overview

Outgassing is the release into vacuum of molecules that were trapped on or in a material. Several types of mechanisms can lead to outgassing, covered by clauses 4.1.2 to 4.1.4.

4.1.2 Desorption

Desorption is the release into vacuum of molecules that were adsorbed on top of a materials. Molecules are initially linked to the material by weak forces (physisorption) or stronger forces (chemisorption). The random thermal movements of a molecule may allow it to leave the resulting potential wall to vacuum.

As a consequence desorption is considered to follow a first order law:

$$\frac{dm^{\alpha}}{dt} = -\frac{m^{\alpha}}{\tau_d^{\alpha}(T)} \qquad \text{[4-1]}$$

with dm^{α}/dt : weight loss per surface unit of species α (g.cm^{-2}·s^{-1})

       m^{α} : contaminant α available mass per surface unit (g·cm^{-2})

       $\tau_d^{\alpha}(T)$: outgassing time constant of species α (s)

       T : temperature (K)

The desorption time constant is thermally activated (Arrhenius law):

$$\tau_d^{\alpha}(T) = \tau_{d0}^{\alpha} e^{-E_d^{\alpha}/RT} \qquad \text{[4-2]}$$

with E_d^{α} : desorption activation energy of species α on this material (kJ/mol)

       τ_{d0}^{α} : Arrhenius pre-exponential factor (s)

       R : the gas constant (0,00831 kJ/mol·K)

In practice these laws are only approximate since many phenomena can complicate things: several types of adsorption sites, interactions with other types of contaminants, etc.

4.1.3   Evaporation

Evaporation is the passage of contaminant from its condensed phase (liquid or solid) to gas phase. The contaminant is thus implicitly assumed to be present as a thick layer on top of the material (many monolayers). For a pure chemical compound evaporation follows zero-order Langmuir law:

$$\frac{dm_{evap}}{dt} = -0.044 \cdot \sqrt{\frac{M}{T}} P_s\left(T\right)$$

[4-3]

with dm_{evap} / dt : evaporation rate per surface unit (g·cm^{-2}·s^{-1})

  M : molar mass (g/mol)

  T : surface temperature (K)

  $P_s(T)$: vapour pressure (mbar), depends on temperature

The numerical coefficient 0,044 becomes 0,058 if P$_s$ is in Torr, and its literal expression is $(2\pi R)^{-1/2}$. The vapour pressure varies with temperature following Clausius-Clapeyron law.

4.1.4   Diffusion

Contaminant molecules can be located deep inside a material. The random motion of these molecules within the material is called diffusion. Those reaching the vacuum exposed surface of the material can further be desorbed to vacuum.

In the simplest cases diffusion obeys Fick's law:

$$f(x) = D\frac{dn(x)}{dx}$$

[4-4]

with f : contaminant flux through the material (g·cm^{-2}·s^{-1})

  n : the contaminant concentration in the material (g/cm^3)

  D : the diffusion coefficient (cm^2/s)

  x : the depth coordinate throughout the material (cm)

The diffusion coefficient is in principle thermally activated (Arrhenius law). In more complex situations diffusion can also be non-fickian.

4.2   Transport

Outgassed molecules travel through vacuum or rarefied gas to reach other surfaces on which they can condensate. In space condition molecular mean free path is usually large (larger than the system) and this transport is mostly line of sight. It can thus involve reflection on surfaces and few collisions in gas phase. Describing transport more in detail is beyond the scope of this technical memorandum.

4.3   Sticking/condensation

At very short time scale a large fraction of molecules impinging a surface is thought to stick, at least very transiently (typically sub picosecond). Although this may not always be true, in particular for suprathermal velocities, short term sticking is often considered to be total (sticking coefficient = 1).

At longer time scale molecules can be re-emitted (desorption, evaporation). If the re-emission time remains small the sticking - re-emission can be considered as a reflection. As a consequence sticking at longer time scale is usually not considered as total. A sticking coefficient S, comprised between 0 and 1, describes the fraction of impinging molecules that remain condensed on the surface. There is no general agreement on its form.

4.4 Re-emission

Condensed molecules can be re-emitted to vacuum. Considering that condensed molecules remain on the material top surface re-emission should be described by desorption (sub monolayer deposit) or evaporation (thick deposit). In case of a mixture of contaminant, Raoult's law should be used to account for mixing effects (limited to an ideal mixture). If condensed molecules undergo diffusion through the material, diffusion should in principle also be taken into account.

In practice re-emission comes after outgassing and condensation and re-emission data are scarce. When non absent, the modelling of re-emission is thus usually limited to a simple law, like first order desorption law:

$$\left(\frac{dm^\alpha}{dt} \right)_{re-emission} = -\frac{m^\alpha}{\tau_r^\alpha (T)} \qquad [4-5]$$

with dm^α / dt : re-emission per surface unit of species α (g·cm^{-2}·s^{-1})

          m^α : deposited mass of contaminant α per surface unit (g·cm^{-2})

          $\tau_r^\alpha (T)$: re-emission time constant of species α (s)

          T : temperature (K)

Re-emission is thermally activated and $\tau_r^\alpha (T)$ follows an Arrhenius law.

5
Test methods available in Europe

5.1 Material samples

5.1.1 Identification of materials

a. Materials submitted for testing shall be accompanied by a completed material identification card in conformance with Annex A.

b. The MIC shall contain the information from the declared material list (DML), where the materials are described for a specific space project, or micro-VCM test results according to ECSS-Q-ST-70-02.

c. Dimensions and mass of the sample and, where applicable, of its holder and/or substrate shall be controlled, measured, and documented.

d. The sample mass should be measured with a microbalance with an accuracy of ±10 µg.

e. Fibre volume and inert filler composition shall be reported when used.

f. Identification markings shall not be applied to the sample, unless it is part of the manufacturing process.

5.1.2 Sampling

5.1.2.1 Preparation

a. If the material is made up of several components, the sample shall be prepared according to the process specification or manufacturer's data.

b. The material sample shall be made according to the same process parameters as the relevant material to be applied for spacecraft use.

> NOTE   Examples of process parameters are curing and baking temperature, duration and pressure.

c. The following material amounts should be used:

  1. mass for bulk material ≥ 30 g

  2. surface for coatings, paints, thin films, adhesives, tapes $\geq$ A4 sheet

  3. volume for foams ≥ 1000 cm^3

> NOTE   The aim is to allow several tests to be performed (e.g. different tests or repetitions of tests).

d. The geometry of the material sample should be representative of its application geometry.

e.   Potting materials and bulky adhesives shall be cast on a PTFE sheet so that a sample of a few millimetres thick can be separated from the PTFE after curing.

f.   Samples of potting materials and bulky adhesives shall be cut into cubes or cylinders by using hollow punch.

> NOTE   Typical dimensions for cubes and cylinders:
> - cubes: 25 mm x 25 mm, thickness : 2 mm
> - cylinders: diameter 30 mm, thickness : 2 mm

g.   Thin films, coatings with or without primers, adhesives and adhesive tapes should be applied to a degreased, dried aluminium foil of known thickness and cut into strips 10 mm wide and 25 mm in length.

h.   In case of non-curing adhesives, the samples shall be applied between thin metal foils and prepared as per 5.1.2.1g.

i.   When materials are prepared on a substrate that is non-metallic, a sample of that substrate shall be tested separately.

j.   Materials where the smallest dimension is less that 1,5 mm, shall be cut into pieces of 10 mm long.

> NOTE   Example of such materials are wires, cables or sleeves.

k.   Test materials containing metal parts should be tested without the metal parts.

> NOTE   Example of such materials are electrical wires or connectors.

l.   If materials containing metal parts cannot be tested without the metal parts, the ratio of metal mass to total mass shall be stated.

m.   When materials cannot be hung or placed directly in the test facility, typically liquids and greases, they shall be placed in a dedicated cup or container.

> NOTE 1   Examples of such cups or containers are shown in Figure 5-1.
> NOTE 2   The provision of an adequate cup is generally not a test's customer responsibility.

| coating type sample | grease type sample |
| oil type sample | oil/grease type sample |
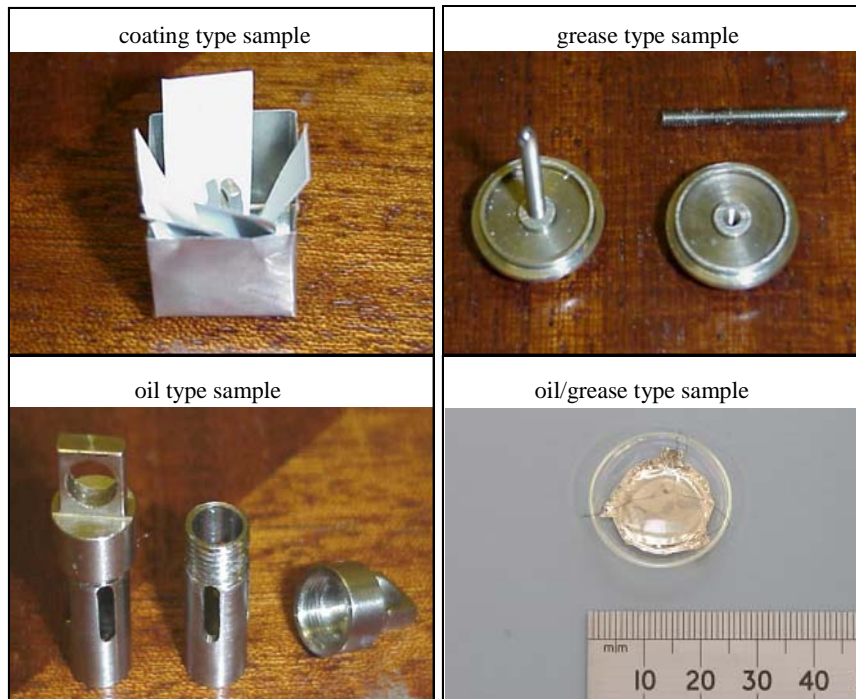
Figure 5-1: Example of shaping of various samples depending on their nature and associated cups

5.1.3 Cleaning

a. The cleaning and any other treatment of the samples shall be the same as that applied to the flight hardware, which the sample is intended to represent, prior to integration into the spacecraft.

b. Material samples shall be tested as received without any further cleaning or treatment, unless otherwise specified by the customer.

5.1.4 Handling and storage

a. No contamination shall be introduced during the handling and storage process.

b. Samples shall only be handled by using tweezers and clean gloves (powder- and lint-free nylon, nitrile or latex).

> NOTE Handling samples with the bare hands could cause false TML and CVCM results due to the oils from the human skin that are usually volatile and condensable.

c. Samples shall be stored in a controlled area, with an room temperature of (22 ± 3) °C and relative humidity of (55 ± 10) % RH.

d. Coated surfaces shall be shielded from contact by using polyethylene or polypropylene bags or sheets.

e. To avoid physical damage, the polyethylene or polypropylene-wrapped workpieces shall be packed in clean, dust- and lint-free material.

f.   Limited-life materials shall be labelled with their shelf life and date of manufacture or date of delivery if date of manufacture is not known.

5.2   The CNES test method

5.2.1   Introduction

A dynamic outgassing test method has been developed at CNES to study the kinetics of outgassing of a sample under vacuum using the system called "SARTORIUS test bench".

This system is based on the use of a vacuum microbalance in order to measure the total mass loss (TML) of the sample.

Several tests are generally performed : a multi-step temperature test where the sample temperature increases from 25 °C to 125 °C by step of 25 °C every 24 hours and three other ones with a time dependent temperature law between room temperature to 125 °C during 12, 18 and 30 hours.

5.2.2   Facilities and equipment

A photograph of the CNES equipment is shown in Figure 5-2.

Figure 5-2: Overview of vacuum chamber and electronic controlling equipment

The apparatus can be described into three parts: a vacuum chamber, a pumping system and control and data acquisition systems. The SARTORIUS system characteristics are listed in Figure 5-3.

The vacuum chamber consists of a stainless steel frame with 8 ultra vacuum feedthroughs for interchange of measurement signals, a glass cover ($\varnothing$: 30 cm ; H: 45 cm), a vacuum microbalance (see technical characteristics on Figure 5-3) and a cylindrical copper effusion cell with an integral heater. A K-type thermocouple monitors the effusion cell temperature from ambient to a maximum temperature

of 150 °C. A K-type thermocouple measures the temperature of a reference sample inside the effusion cell.

The chamber is equipped with a backing pump, a turbo molecular pump and a cold cathode gauge (Penning vac transmitter) for pressure measurement so that the vacuum chamber provides a pressure lower than 10^{-4} Pa within one hour of pumping. A sputter-ion pump could be used for very long tests. A high-vacuum gate valve is used to isolate the chamber and to maintain the sample under static vacuum.

> NOTE A Residual Gas Analyser (RGA) could be used to follow the partial pressure of identified gases during the test.

An electrical cabinet consists of a stabilized power supply (for heater, transmitter electronics), a data acquisition system for pressure, temperature and mass measurements, the electronic parts of the vacuum microbalance, a temperature controller. A computer interfaced with the data acquisition system performs the acquisition scanning at different defined intervals and stores the data.

Vacuum microbalance
SARTORIUS type 4410 MP8
Maximum loading mass : 25 g

range	I	II
TML max (mg)	1100	200
Readability (µg)	10	1

Effusion cell
∅ : 50 mm ; L : 45 mm
orifice : 10 mm
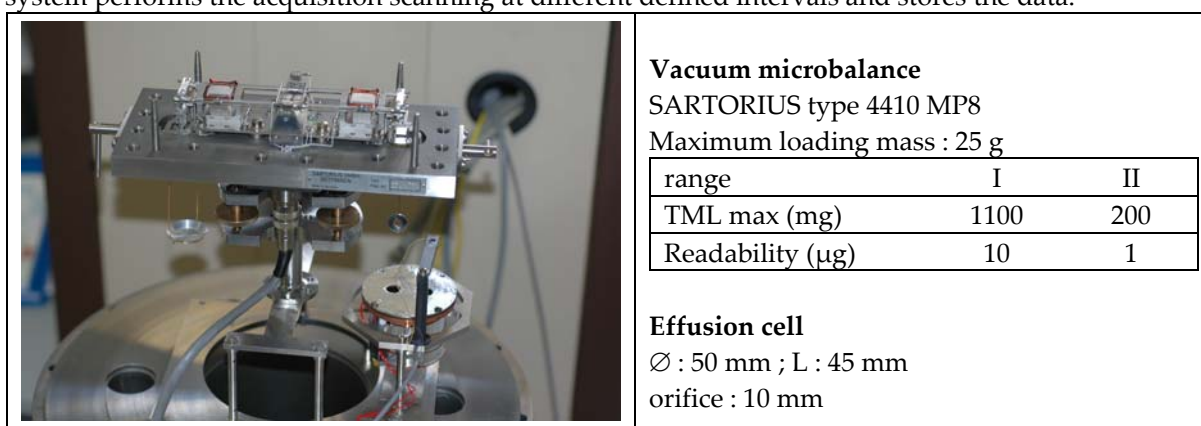
Figure 5-3: Overview of SARTORIUS balance and technical characteristics

Support equipment /materials are:

- analytical microbalance - typically SARTORIUS MC 21 S with a capacity of 21 g, a readability of 1 µg, and a linearity of 15 µg (to weigh the samples before and after test and conditioning)

- high purity, low NVR solvents (to clean the effusion cell and other hardware before test) Suitable reagent grade solvents include acetone, IPA, chloroform and ethanol.

- powder and lint-free gloves (nylon, nitrile or latex)

- micrometer (to measure sample dimensions)

- dry GN2 (99,9% pure or better) (to backfill the chamber)

- oven (e.g. for the conditioning of cups)

5.2.3   Test method

The test method uses the SARTORIUS test bench described in clause 5.2.2.

Depending on the nature and the shape of the sample, either the material or the cup is hung from the vacuum microbalance.

Four tests are necessary for the comparative outgassing study:

- three tests are based on a time dependent temperature law between room temperature to 125 °C during 12 h, 18 h and 30 h.

- another one is a multi-step temperature test where the sample temperature increases from 25 °C to 125 °C by step of 25°C every 24 hours.

5.2.4 Test protocol

5.2.4.1 Sample pre- and post-conditioning

Prior to any test, the sample is conditioned at (22 ± 3) °C and a relative humidity of (55 ± 10) % for at least 24 hours.

After the test, the sample is re-placed in the same conditioned environment in order to measure the recovered mass loss (RML).

5.2.4.2 Test execution

The main steps of the test method are:

- Bake the cups for a couple of hours at 100 °C in an oven

- Clean the test chamber components (effusion cell, specimen cups, screen…) with a compatible solvent

- Weigh the sample before its conditioning for 24 hours at (22 ± 3) °C and (55 ± 10) % RH with an external analytical microbalance located in the same room at the same ambient conditions

- Control the data acquisition system

- Switch on the vacuum microbalance

- Weigh the sample with the external microbalance after its conditioning

- Lock the vacuum microbalance and install the sample onto its hook

- Unlock the balance and select the correct range according to Figure 5-3

- Close the chamber

- Start the data acquisition system and control the first measured data at atmospheric conditions : temperature of the sample, of the effusion cell, mass

- Start pumping down

- Select and start the temperature program depending on the test (multi-step test or test with defined slope)

- After test exposure, stop pumping and the temperature program ; when the temperature of the effusion cell is at 25 °C, vent up the system to atmospheric pressure with GN_2

- Lock the balance and open the chamber

- Remove the sample and weigh it with the external microbalance

- Weigh the sample with the external microbalance after a new conditioning for 24 hours at (22 ± 3) °C and (55 ± 10) % RH

- Clean the test chamber components

5.2.5 Measurements / Data processing

5.2.5.1 Measurements

For each temperature program applied for the test method, the time evolution of the TML is measured with the vacuum microbalance (see Figure 5-4 with HYSOL EA 9321 as test material).
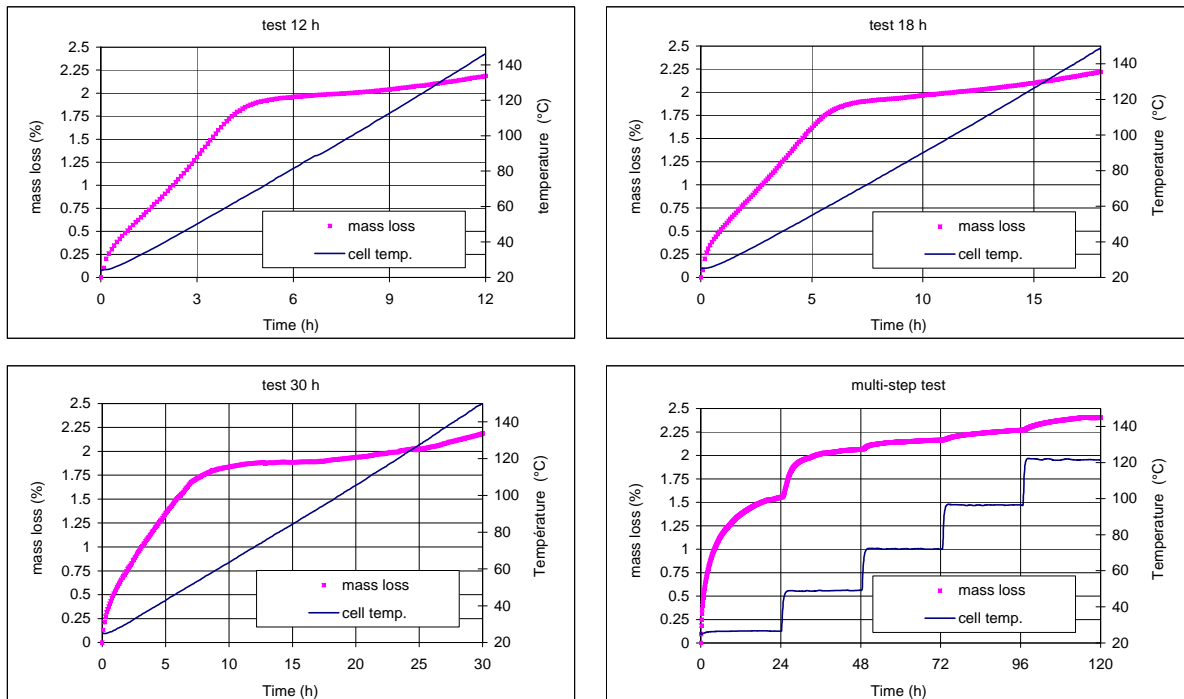
Figure 5-4: Outgassing tests for HYSOL EA 9321

At the end of each test, the sample is also weighted with an external analytical balance in order to compare the measurements.

After 24 hours of conditioning at (22 ± 3) °C and (55 ± 10) % RH, the RML is measured with the external balance and the WVR is deducted with respect to the following equations:

— TML [%]=100 × ($m_s(i)$-$m_s(f)$)/ $m_s(i)$

— RML [%]=100 × ($m_s(i)$- $m_s(c)$)/ $m_s(i)$

— WVR [%]=TML [%] - RML [%]

with $m_s(i)$: initial mass of the sample (g)

$m_s(f)$: mass of the sample at the end of the test (g)

$m_s(c)$: mass of the sample at the end of the test, after 24 hours of conditioning (g)

5.2.5.2 Buoyancy correction

If the sample density is different from the counterbalance used for equilibrium, a buoyancy effect occurs during the depressurization and cause systematically a measurement error, as a change of the mass measurement. Its range is dependent on the density of the sample.

> NOTE   If a sample highly outgases at depressurization, the buoyancy effect may be offset by the mass loss of the sample itself and may not appear on the measurements.

To estimate the shift range and correct the results, it is necessary to reduce the interval of measurements during the beginning step and during the venting step in order to compare the mass loss measured with the vacuum balance (m_3 - m_0) to the mass loss measured with an external analytical balance (m_f - m_i) as described in Table 5-1. If the results are consistent, all the measurements are corrected taking into account the quasi-instantaneous mass shift at the end of the venting step.

<p style="text-align:center">Table 5-1: Mass measurements</p>

External analytical balance	before test: initial mass (m_i)
	after test: final mass (m_f)
	total mass loss = m_f - m_i
Vacuum balance	initial mass after equilibrium at atmospheric pressure: m_0
	mass at the beginning of depressurization: m_1 negative zero shift; positive mass loss
	mass at the end of test: m_2
	mass after venting with GN_2 (m_3) positive zero shift; sample mass loss $\approx$ 0 at the end of the test
	total mass loss = m_3 - m_0 mass shift = m_3 - m_2 ($\geq m_1$ - m_0)

5.2.5.3 Reporting of test data

Results are reported in a test report.

5.3 The ESTEC test method

5.3.1 Introduction

The test method defined at ESTEC to study the kinetics of the outgassing of a sample and of the deposition of the contaminants under vacuum utilizes systems called VBQC (Vacuum Balance Quartz Crystal) and DOK (Dynamic Outgassing Knudsen cell).

The systems are based on the use of QCMs (Quartz Crystal Microbalances) to measure the CVCM (Collected Volatile and Condensable Materials) coming from the sample, coupled with an other QCM (for the DOK system) or a vacuum balance (for the VBQC system) to measure the TML (Total Mass Loss) from the sample due to outgassing.

The standard test performed with these systems is a multi-step temperature test where the sample temperature is increased from 25 °C to 125 °C by step of 25 °C every 24 hours.

5.3.2   Test facilities and equipment

5.3.2.1   Overview

ESTEC uses 3 facilities to perform dynamic outgassing tests. These facilities are so called:

- VBQC2

- VBQC3

- DOK

5.3.2.2   VBQC2 and VBQC3

VBQC2 and VBQC3 are based on the same apparatus that consists of a vacuum chamber, a temperature control system, a vacuum microbalance, three QCMs and a data acquisition system. The schematic of the facility is shown in Figure 5-5.

The QCMs are used to measure the CVCM and the vacuum balance to measure the TML.

The VBQC system is equipped with a backing pump and a turbo pump and associated gauges (pirani and cold cathode gauges). The vacuum chamber provides a pressure lower than $5 \cdot 10^{-4}$ Pa.
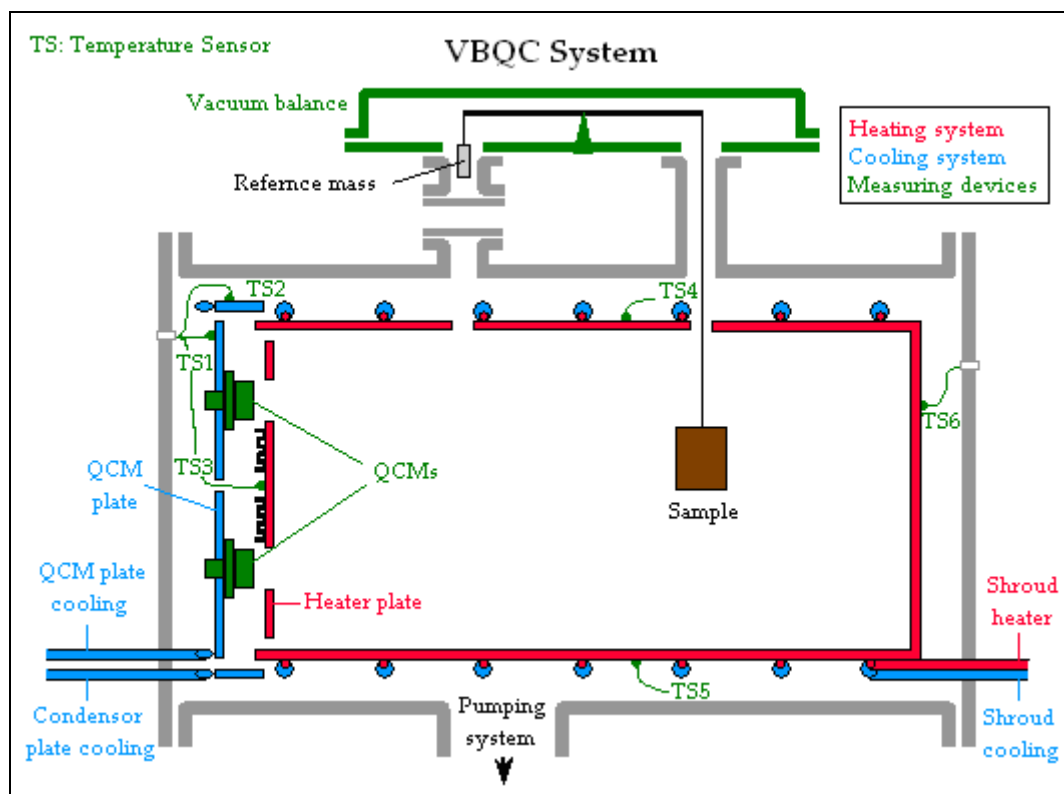
Figure 5-5: VBQC system schematic

The heating system is used to heat the sample by radiation. It is divided in two parts: the main shroud and the heater plate. In both parts the temperature is controlled and measured using temperature sensors (Pt100) associated with a controller device.

The cooling system is composed of the QCM plate on which the QCMs are mounted, the condenser plate (VBQC3 only) and the shroud cooling.

The QCM plate is used to cool down the QCMs using a cryostat bath. The condenser plate is used as contaminant trap, and is cooled down using a cryostat bath as well. The cooling shroud is normally not used but allows cooling down the sample to start at a lower temperature than room temperature.

The QCMs are built with Peltier or heater element inside which allows cooling down or heating up of the QCM relative to the temperature of the QCM plate.

The VBQC system characteristics are listed in Figure 5-6.

VBQC 2				**VBQC 3**		
Vacuum microbalance				**Vacuum microbalance**		
SARTORIUS type 4433				SARTORIUS type M 25D-V		
Maximum loading mass: 2,54 g				Maximum loading mass: 28 g		
range	I	II	III	Range	I	II
TML max (mg)	280	28	2.8	TML max (mg)	1100	200
Readability (µg)	10	1	0,1	Readability (µg)	10	1

3 QCMs
Mark 10 Thermoelectric Quartz Crystal Microbalance (MK10 TQCM™), 15 MHz crystal. Each QCM contains two crystals (one for mass collection and one for reference), the oscillator electronics, and a temperature sensor (Pt100).
Sensitivity: $1,96 \cdot 10^{-9}$ g/Hz $\cdot$ cm²
Peltier element built inside

3 QCMs
Mark 10 Thermoelectric Quartz Crystal Microbalance (MK10 TQCM™), 15 MHz crystal. Each QCM contains two crystals (one for mass collection and one for reference), the oscillator electronics, and a temperature sensor (Pt100).
Sensitivity: $1,96 \cdot 10^{-9}$ g/Hz $\cdot$ cm²
Peltier element built inside

Figure 5-6: VBQC2 and VBQC3 characteristics

A computer interfaced (via RS232) with a data acquisition control unit performs the acquisition scanning at the desired interval. The computer also controls the sample temperature changes.

5.3.2.3 DOK

The DOK (Dynamic Outgassing Knudsen cell) facility has been designed according to ASTM E-1559 and consists of a vacuum chamber, a vacuum interlock chamber, a temperature control system, an effusion cell (Knudsen cell), four Quartz Crystal Microbalances (QCM's), a Residual Gas Analysis (RGA) and a data acquisition system.

Three QCMs are used to measure the CVCM. A fourth QCM, so called "cryoQCM" because it is maintained at cryogenic temperature, measures the TML.

Figure 5-7 shows a picture of the DOK apparatus. The main chamber is equipped with a backing pump and a turbo pump and associated gauges (pirani and cold cathode gauges). The main vacuum chamber provides a pressure in the range of 10^{-6} Pa.

A high-vacuum gate valve is used to isolate the main chamber from the interlock chamber and allows withdrawing and inserting the Knudsen cell into the main chamber without the loss of high vacuum in the main chamber. The interlock is equipped with a backing pump that allows reaching a primary vacuum.

Two QCMs are mounted at 20° and two at 10° with respect to the normal of the cell orifice, so that the active surface of any QCM cannot "see" the active surface of any other QCM. The QCM that is operating at cryogenic temperature for measuring the total outgassing rate is installed on a cryo plate cooled down via liquid Nitrogen. The other three QCMs are operating at defined temperatures for the

measurement of the deposition of outgassing condensable. These are installed on a plate thermally decoupled from the QCM cryo plate and cooled down by a cryo-bath.

The shroud and the QCM cryo-plate are cooled down via liquid Nitrogen.

The Knudsen cell is cylindrical and has an integral heater capable of uniformly heating the cell itself up to 500 °C.

The RGA is used to identify the gases present in the vacuum during the execution of the test.

Three Pt100s monitor the temperature of the cryo-shroud, the QCM cryo-plate and the QCM cold plate. Three K-type thermocouples measure the Knudsen cell temperature in three different spots.
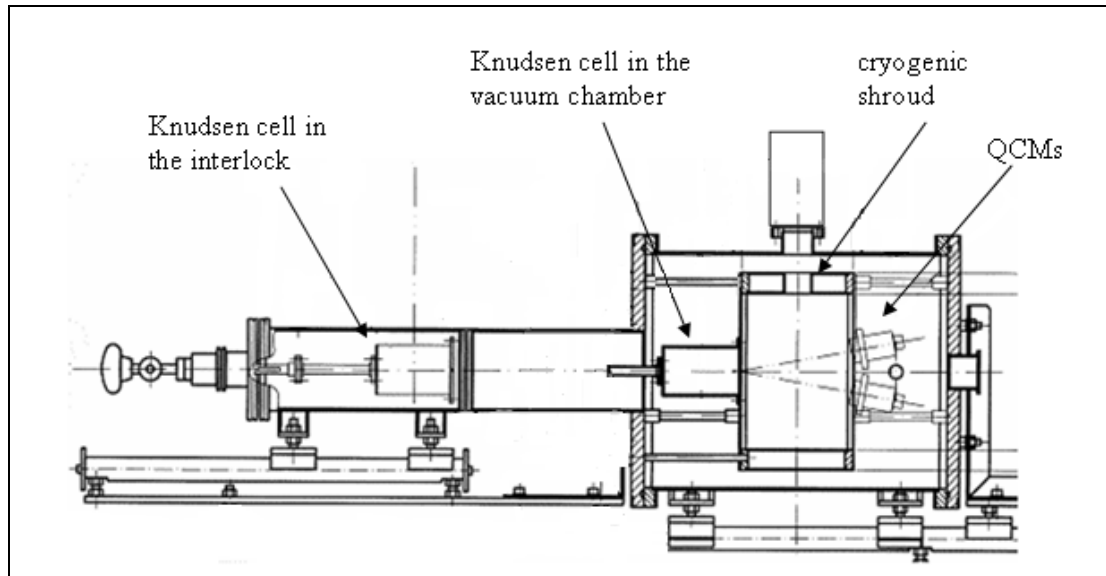
Figure 5-7: DOK schematic

The DOK system characteristics are listed in Figure 5-8.

DOK

Knudsen cell
Ø 60 x L 95 mm
Orifice: Ø 3 mm
Maximum loading mass: 500 g

4 QCMs
Mark 10 Thermoelectric Quartz Crystal Microbalance (MK10 TQCM™), 15 MHz crystal. Each QCM contains two crystals (one for mass collection and one for reference), the oscillator electronics, and a temperature sensor (Pt100).
Sensitivity: $1,96 \cdot 10^{-9}$ g/Hz · cm^2
Peltier element built inside

Figure 5-8: DOK characteristics

A computer interfaced (via RS232) with a data acquisition control unit performs the acquisition scanning at the desired interval. The computer also controls the sample temperature changes.

5.3.2.4   Support equipment and materials

- Analytical microbalance - with a 200 g or greater tare, a readability of 10 μg or better is required for recording mass changes of the samples

- Oil-free aluminium foil - non-outgassing substrate/shielding material

- Gloves - powder- and lint-free nylon, nitrile or latex

- Micrometer - to measure sample dimensions

- Low NVR IPA and swabs (with a low NVR) - to clean QCM surfaces

- Dry GN_2 (99,9% pure or better) - to backfill the interlock chamber/main chamber.

5.3.3   Test methods

5.3.3.1   Overview

There are two dynamic outgassing test methods: the VBQC test method and the DOK test method.

At the end of a dynamic outgassing test thermogravimetric measurements are performed.

5.3.3.2   The VBQC test method

The VBQC test method uses the VBQC systems, described in clause 5.3.2. The sample is hanged from the vacuum microbalance and in line of sight of the QCMs. The size of the sample should not exceed 12x12 cm and the maximum loading mass, given in Figure 5-6. In order to obtain the highest accuracy, based on the mass of the sample (TML given in %) or on the surface of the sample (TML given in mg/cm2), it is recommended to have a sample close to the maximum size or mass. However a sample which is representative for the actual used hardware is recommended.

The VBQC test is a multi-step temperature test where the sample temperature is increased from 25 °C to 125 °C by step of 25 °C every 24 hours.

All QCMs are cooled using a cryostat bath and stabilized at -25 °C, -50 °C and -75 °C with Peltier elements. The test duration is 120 hours.

A blank test is run at the some conditions prior to the outgassing test in order to measure the facility background and subtract the chamber contribution to the sample data. During the blank preparation, the vacuum chamber is empty and handled as if a sample were to be hanged.

5.3.3.3   The DOK test method

The DOK test method uses the DOK system, described in clause 5.3.2. The sample is placed in the Knudsen cell via the interlock chamber and then introduced into the main chamber at a pre-defined distance and angle with respect to the QCM surfaces. The sample size and weight should not exceed the Knudsen cell specifications, given in Figure 5-8. In order to obtain the highest accuracy, based on the mass of the sample (TML given in %) or on the surface of the sample (TML given in mg/cm2), it is recommended to have a sample close to the maximum size or mass. However a sample which is representative for the actual used hardware is recommended.

The DOK test, like the VBQC one, is a multi-step temperature test where the sample temperature is increased from 25 °C to 125 °C by step of 25 °C every 24 hours.

Three QCMs are cooled using a cryostat bath and stabilized at -25 °C, -50 °C and -75 °C with Peltier elements. The fourth QCM is maintained at liquid Nitrogen temperature (-177 °C) for the measurements of the TML. The shroud is maintained at -175 °C.

The test duration is 120 hours.

A blank test is run at the same conditions prior to the outgassing test in order to measure the facility background and subtract the chamber contribution to the sample data. During the blank preparation, the effusion cell is empty and handled as if a sample were to be loaded.

5.3.3.4   QCM TGA measurements

QCM TGA measurements are performed at the end of the outgassing test in order to retrieve additional information on the composition of the outgassed/condensed contaminants. It consists in the evaporation from the surface of each QCM, one by one at a specific rate and starting from the coldest one, of deposited contaminants.

5.3.4   Test protocols

5.3.4.1   Sample pre- and post-conditioning

Prior to any test, the sample is conditioned at (22 ± 3) °C and a relative humidity of (55 ± 10) % for at least 24 hours.

After the test, the sample is re-placed in the same conditioned environment in order to measure the recovered mass loss (RML).

5.3.4.2   Test execution

5.3.4.2.1   VBQC test method

The main steps of the VBQC test methods are:

- Clean the test chamber components before assembly

- Weigh the sample, previously conditioned at (22 ± 3) °C and (55 ± 10) % RH for at least 24 hours, according to 5.3.4.1, with an external analytical balance

- Install Al foil for subsequent FTIR and/or GC/MS analyses

- Lock the vacuum microbalance and install the sample onto its hook

- Unlock the vacuum microbalance and select the correct range according with Figure 5-6

- Close the VBQC facility

- Connect the QCM and temperature cables

- Connect the cooling bath to the QCM plate

- Start the data acquisition program: the sample temperature is controlled by the computer according to the following: 24 h @ 25 °C, 24 h @ 50 °C, 24 h @ 75 °C, 24 h @ 100 °C, 24 h @ 125 °C, i.e. 120 hours in total

- Measure the first data point at atmospheric conditions

- Start pumping down

- When pressure is in the range of $1 \cdot 10^{-2}$ Pa, start cooling the cryobath to -80 °C

- Start cooling the QCMs at 1°C/min to -25 °C, -50 °C, -75 °C respectively

- After 120 hours of dynamic outgassing test, the program will set the sample temperature to 20 °C

- When the sample temperature is at 40°C, start TGA of QCMs at 1°C/min:

    1. first from -75 °C to 80 °C,

    2. second from -50 °C to 80 °C, and

    3. finally from -25 °C to 80 °C

- At the end of QCM TGAs set QCMs to 20 °C at 7 °C/min

- When the QCMs are at 20 °C, stop pumping and venting with GN_2

- When chamber is re-pressurised, set cooling bath to +20 °C

- When the cooling bath is at 20 °C, lock the balance and open the VBQC facility

- Remove the sample and weigh it with an external analytical balance

- Place the sample into an environmentally controlled cabinet with (22 ± 3) °C and (55 ± 10) % RH, according to 5.3.4.1

- Remove the Al foil and store it into clean container for GC/MS and/or FTIR analyses

- Take a rinse of the QCM plate with IPA and collect it into a clean petri-dish for FTIR analysis

- Perform a cleaning of the facility

5.3.4.2.2   DOK test method

The main steps of the DOK test methods are:

- Clean the test chamber components before assembly

- Install Al foil for subsequent FTIR and/or GC/MS analyses

- Start pumping down

- When the pressure is in the range of $1 \cdot 10^{-2}$ Pa, set the cooling bath to -40 °C

- When the cooling bath is at -40 °C, set the shroud to -175 °C

- When the shroud is at -175 °C, set the cryoQCM plate to -177 °C

- Set the QCMs' temperatures to -25 °C, -50 °C, -75 °C at 7 °C/min

- Weigh the sample, previously conditioned at (22 ± 3) °C and (55 ± 10) % RH for at least 24h, according to 5.3.4.1, with an external analytical microbalance

- Vent the interlock chamber with clean, dry GN_2

- Open the load port of the interlock chamber and open the effusion cell; continue to purge the interlock chamber with GN_2

- Place the test sample in the effusion cell and close it

- Start the data acquisition program and verify that the QCMs and the data acquisition system are operating properly. The sample temperature is controlled by the computer according to the following: 24 h @ 25 °C, 24 h @ 50 °C, 24 h @ 75 °C, 24 h @ 100 °C, 24 h @ 125 °C, i.e. 120 hours in total

- Move the effusion cell into the main chamber

- After 120 hours of dynamic outgassing test, the program will set the temperature of the effusion cell to 20 °C

- Move the effusion cell to the interlock chamber

- Backfill the interlock chamber with clean, dry GN_2

- Remove the sample and weigh it with an external analytical balance

- Place the sample into an environmentally controlled cabinet with (22 ± 3) °C and (55 ± 10) % RH, according to 5.3.4.1

- start TGA of QCMs at 1°C/min:

  1. first from -75 °C to 80 °C,

  2. second from -50 °C to 80 °C, and

  3. finally from -25 °C to 80 °C

5.3.4.3 Facility and hardware cleaning

a. The work area shall be air filtered and clean from dust as achieved with normal house-keeping.

b. All vacuum systems shall be cleaned in accordance with good vacuum practices before assembly.

c. The facility shall be cleaned by wiping the internal surfaces with acetone first and then IPA and by performing a dedicated vacuum bake-out using the internal shroud (when it is part of the system) and external heaters.

d. In case there is still residue on the QMC crystal after heating with the Peltier element only, the crystal should be physically cleaned using alcohol or hexane dipped Q-tip and brushing the crystal very lightly.

> NOTE   It can happen that the deposition of some contaminants onto the QCM crystal can result in an undesirable residue, which might be impossible to clean by vacuum bake-out using the Peltier element only.

e. Acetone shall never be used in the physical cleaning of the QCM crystal.

5.3.4.4 Reporting of test data

Results are reported in a test report.

5.3.5 Measurements/Data processing

5.3.5.1 VBQC test method

With the VBQC test method the time evolution of the TML is measured with the vacuum balance and compared with the measurements of the external analytic balance. The RML and WVR are measured with the external analytic balance only.

The following equations are used:

$\quad$— $\quad$ TML[%] = 100 × $(m_s(i) - m_s(f)) / m_s(i)$

$\quad$— $\quad$ RML[%] = 100 × $(m_s(i) - m_s(c)) / m_s(i)$

$\quad$— $\quad$ WVR[%] = TML[%] - RML[%]

with $\quad m_s(i)$: initial mass of the sample (g)

$\quad m_s(f)$: mass of the sample at the end of the test (g)

$\quad m_s(c)$: mass of the sample at the end of the test, after 24 hours of conditioning (g)

The time evolution of the CVCMs is measured with the three QCMs and calculated with the following equation:

$$CVCM\ [\%] = 100 \times \left[\frac{VF \cdot K_s \left[f(T_q, T_s, t) - f(T_q, T_s, 0) \right]}{m_s(i)} \right]$$

with   VF: view factor of the QCM (cm²)

K_s: QCMs mass sensitivity factor (g·cm⁻²·Hz⁻¹)

$f(T_q, T_s, t)$: QCM frequency at time t (Hz)

$f(T_q, T_s, 0)$: QCM frequency at time 0 (Hz)

$m_s(i)$: initial mass of the sample (g)

5.3.5.2   DOK test method

With the DOK test method the time evolution of the TML is measured with the cryo-QCM and compared with the measurements of the external analytic balance. The RML and WVR are measured with the external analytic balance only and calculated according to the equations in paragraph 5.3.5.1.

The following equation is used for the calculation of the TML:

$$TML\ [\%] = 100 \times \left[\frac{VF_{cryo} \cdot K_s \left[f(T_q, T_s, t) - f(T_q, T_s, 0) \right]}{m_s(i)} \right]$$

with VF_{cryo}: view factor of the cryo-QCM to the effusion cell orifice (cm²)

K_s: cryo-QCM mass sensitivity factor (g·cm⁻²·Hz⁻¹)

$f(T_q, T_s, t)$: cryo-QCM frequency at time t (Hz)

$f(T_q, T_s, 0)$: cryo-QCM frequency at time 0 (Hz)

$m_s(i)$: initial mass of the sample (g)

The time evolution of the CVCMs is measured with the three (non cryogenic) QCMs and calculated as for the VBQC method, see paragraph 5.3.5.1.

5.3.5.3   Corrections

All mass measurements are corrected for drift, in the case of the balance, and by subtracting the background measurements, in the case of QCMs; both balance drift and QCMs' background measurements are taken during a blank test.

The mass values measured by the vacuum balance in the VBQC test method are also corrected for the buoyancy effect. The initial mass is considered to be the first value measured after depressurisation of the chamber, whilst the final mass is the last value before re-pressurisation.

6
The ASTM test method

The ASTM test method for dynamic outgassing is fully described in ASTM E1559-09, Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials. In brief, the method consists in measuring on QCMs the deposition of contaminants originating from a sample material in an effusion cell. The temperatures of the outgassing material and of the QCMs are maintained constant over a few days. Different temperatures are tested for the emitter and the receiver. QCM TGA measurements are usually performed at the end of the test to obtain information on the volatility of the condensed contaminants.

Two test methods are defined, Test Method A, the standard procedure that uses prescribed configurations and temperatures, and Test Method B, allowing for the use of spacecraft system specific temperatures, configurations, and QCM collector surface finishes. The methods defined in this standard can be used to produce the data necessary to support mathematical models used for the prediction of molecular contaminant generation, migration, and deposition.

The approach provided by the ASTM standard for the contamination assessment for a space mission is a direct empirical approach based on test results. Worst case temperatures are selected in the datasets with respect to flight data, i.e. the next warmer temperature for the source and the next colder for the deposition surface. The corresponding experimental data, extending over a few days, are then mathematically extrapolated to many year missions, through some power law or logarithmic law.

7
Extraction methods for model parameters

7.1 Introduction

The physical equations of clause 4 have many parameters, specific to each species and material. Contrarily to most aspects of transport, the determination of these parameters for outgassing, deposition and re-emission necessarily relies on experiments.

Historically the first tests were focussed on outgassing. Fitting TML curves by outgassing laws led to optimal outgassing parameters. Outgassing was usually modelled through the desorption of about six pseudo-species (cf. clause 7.2). In numerical tools sticking was often supposed perfect (as e.g. in Outgassing, clause 8.2) while re-emission parameters were rather arbitrarily derived from outgassing ones.

When dynamical CVCM data became available, the characterisation of condensation was made possible. Clause 7.3 reports how outgassing and condensation parameters were extracted from CVCM curves for COMOVA code (clause 8.1) consistently with its governing equations. By lack of data re-emission remained crudely assessed.

Finally the emergence of re-emission data, typically through TGAs, shall lead to a very significant improvement, both of the re-emission modelling and of the species separation. The state of the art of this new approach is briefly sketched in clause 7.4.

7.2 Outgassing (no condensation / re-emission)

7.2.1 The CNES method

A method has been defined at CNES to determine, for a given material, a coherent set of outgassing kinetic coefficients from different tests results. A software called LP/VB5E has been developed and is used for the extraction of the outgassing parameters and the simulation of different isothermal outgassing kinetics. Its characteristics and inputs and outputs are described in Table 7-1. Globally, these results allow analysing the outgassing behaviour of a material under vacuum and different thermal constraints and durations and predicting the effect of a pre-treatment.

Table 7-1: LP/VB5E software characteristics

environment	Windows
language	Visual Basic 5
inputs	Post-processed test results time (s) ; mass loss (%) ; sample temperature (K)
outputs	- Coefficients (μ, E, A, τ)$_{1\,to\,5}$ - 2D graphs : TML vs. time TML$_{expo\,(i)}$ vs. time - 3D graphs : TML vs. (temperature, time)

The LP/VB5E software consists of three parts: computation, simulation and database.

The 'computation part', based on different hypotheses (first order desorption law, consideration of 5 outgassed chemical species with decreasing volatility, linear temperature slope), enables to find the coefficients (μ, E, A)$_{1\,to\,5}$ from the multi-step test (see Figure 7-1) according to the basic equations of the Table 7-2. These coefficients are adjusted to minimise the mean squared error (MSE) of the other test results ('test 12 h', 'test 18 h', 'test 30 h'). Then the results are synthesised to extract the mean coefficients with their uncertainties.

The 'simulation part' enables to simulate outgassing graphs for a given material (see Figure 7-2) using either CNES inputs (coefficients (μ, E, A)$_{1\,to\,5}$) or ESABASE/outgassing software inputs (coefficients (μ, E, τ)$_{1\,to\,5}$) with different temperature profiles (e.g. isothermal, multi-step or slope profiles). The simulated tests can be compared to the real tests.

All the results are stored in a database in such a format to be re-used for other computation.

Table 7-2: basic equations used in LP/VB5E software

mass equation for a chemical species i	$\dfrac{d\mu_{i(t)}}{dt} = k_{i(t)}(\mu_i - \mu_{i(t)})$ $initial\ conditions$ $\mu_{i(t_0)} = 0$
Arrhenius law	$k_{i(t)} = A_i e^{-E_i/RT_{(t)}}$
time constant at reference temperature	$\tau_{i(t)} = 1/k_{i(t)}$
solution of the mass equation for n chemical species	$\mu_{(t)} = \displaystyle\sum_{i=1}^{n} \int_{t_0}^{t} (\mu_i - \mu_{i(t)}).(1 - e^{k_{i(t)}dt})$

with   i : index of species

n: number of chemical species

$\mu(t)$: outgassed total mass (%)

μ_i : initial mass that could be potentially outgassed (%)

$\mu_i(t)$: outgassed mass at time t (%)

$k_i(t)$: rate constant at time t (s^{-1})

τ_i: outgassing time constant at reference temperature (s)

A_i : pre factor (s^{-1})

E_i : activation energy (cal·mol^{-1})

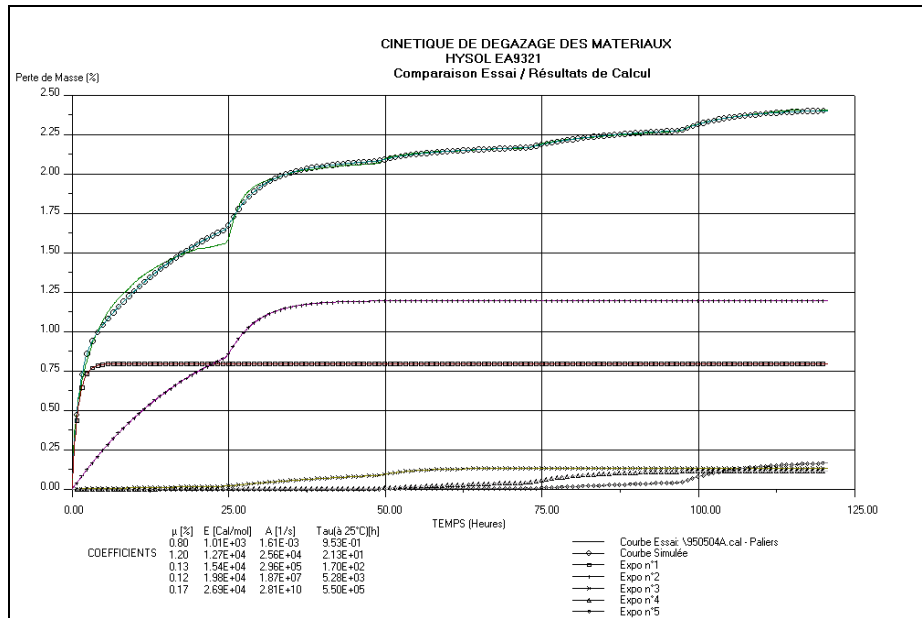R : gas constant (R= 1,986 cal·mol^{-1}·K^{-1})

T : temperature (K)

Figure 7-1: Example of compared test results and simulated results (material HYSOL EA 9321)
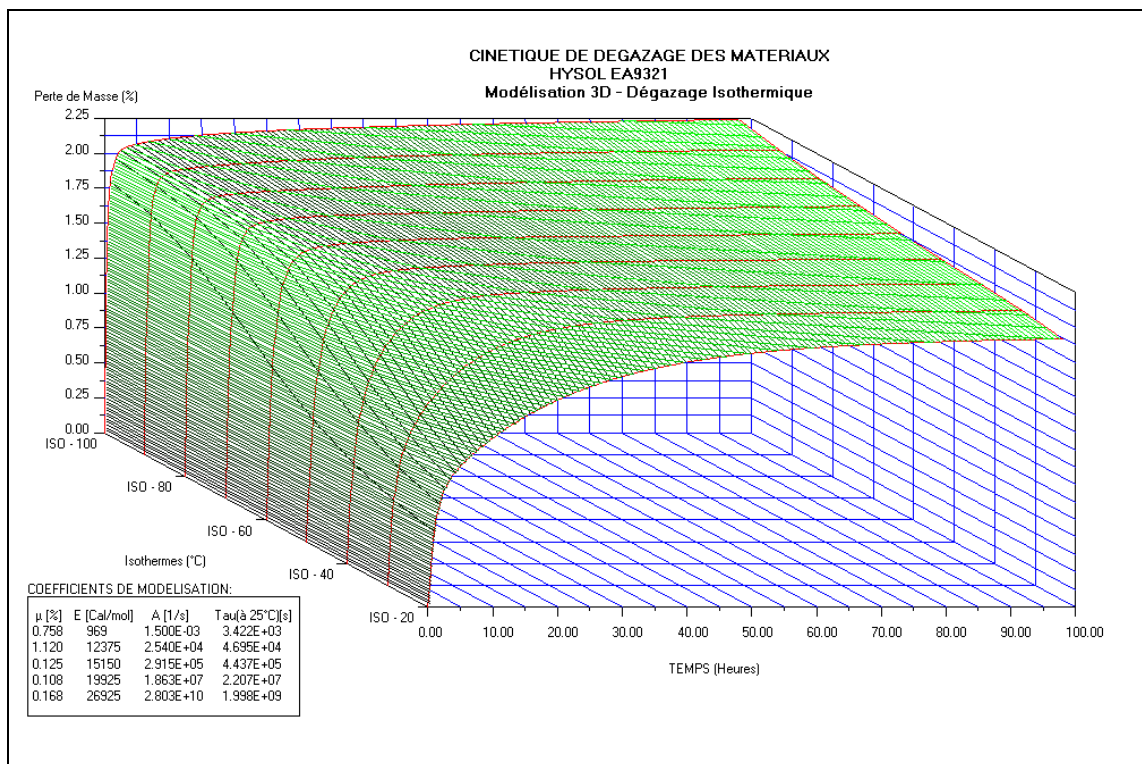

Figure 7-2: Simulation of isotherms (material HYSOL EA 9321)

7.2.2   The ESTEC method

7.2.2.1   Introduction

In the past years, the mathematical treatment of data obtained from dynamic outgassing tests was performed through different Microsoft® Excel worksheets. The execution of the complete sequence required rather lot of manual intervention guided by a work instruction procedure but also requiring subjective operator decisions.

To allow a more straightforward and standardized data treatment, minimizing the manual intervention and the risk behind subjective choices without however loosing the control of the process, a MATLAB® application has been recently developed and its major process steps are described in the following clauses.

7.2.2.2   The data input step

The input data file that contains measurement data for the complete test is loaded by the application and split into the single isothermal steps of the test. Mass losses are referred to the initial sample mass and TMLs over time are computed.

7.2.2.3   The data fitting step

The TML for each isothermal step is analysed by the software and data corresponding to temperature transients (at the beginning of each step) are systematically discarded. Remaining data are fitted with a sum of exponential equations of the form:

$$TML = \sum_i m_{0,i} \cdot (1 - \exp^{-t/\tau_i})$$

[7-1]

with $m_{0,i}$: the initial mass of species i contributing to the outgassing (g)

t : time (s)

τ_i : outgassing time constant of species i (s)

Usually 6 chemical species, with decreasing volatility, are considered.

7.2.2.4   The calculation of acceleration factors and activations energies

For each temperature increase, an acceleration factor K_a is calculated by dividing the TML rate at the beginning of the new step and the TML rate at the end of the previous one.

According to the expression of the acceleration factor that is obtained combining equations [4-1] and [4-2] for two different temperatures:

$$k_a = \frac{\left(\dfrac{dm}{dt}\right)_{T_2}}{\left(\dfrac{dm}{dt}\right)_{T_1}} = e^{\frac{E_a}{R}\left(\frac{T_2-T_1}{T_1 \cdot T_2}\right)}$$

[7-2]

with k_a : acceleration factor

$\dfrac{dm}{dt}$: TML rate (g·s^{-1})

T : temperature (K)

E_a : 'averaged' (as for a single component composition) activation energy (kJ/mol)

R : the gas constant (0.00831 kJ/mol·K)

the activation energy E_a, for each temperature change, is calculated.

7.2.2.5   The long-term predictions step

For each isothermal step j, an accelerated time can be calculated from the acceleration factors by means of the following equation:

$$t_{acc,T_j} = t_{T_j} + \sum_{k=j+1}^{n} \left(t_{T_k} \cdot \prod_{m=j+1}^{k} (k_a)_{T_m,T_{m-1}} \right)$$ [7-3]

with t_{acc,T_j} : accelerated time at temperature T_j

t_{T_j} : actual time at temperature T_j

t_{T_k} : actual time at temperature T_k for each step k that follows step j

n : total number of temperature steps

k_a : acceleration factor

In the standard routine, the temperature of the first step (namely 25 °C) is defined as the reference temperature T_{ref} and an accelerated time is calculated for T_{ref} only. An accelerated isothermal TML at T_{ref} is then obtained by coupling the TML data actually measured all along the test and the accelerated time.

The new curve is fitted with a sum of exponential equations of the same form of equation [7-1] so that a new set of $m_{0,i}$ and τ_i can be calculated for the long-term predictions at T_{ref}.

Finally, for each species i, time constants at different temperatures (typically the ones of the test) are calculated with the following formula:

$$\tau_T = \tau_{T_{ref}} \cdot e^{-k_e \left(T - T_{ref} \right)}$$ [7-4]

that is based on the empirical law:

$$\ln k_a = k_e \cdot \left(T - T_{ref} \right)$$ [7-5]

and long-term prediction curves are computed for the same set of temperatures, as shown in the example of Figure 7-3.
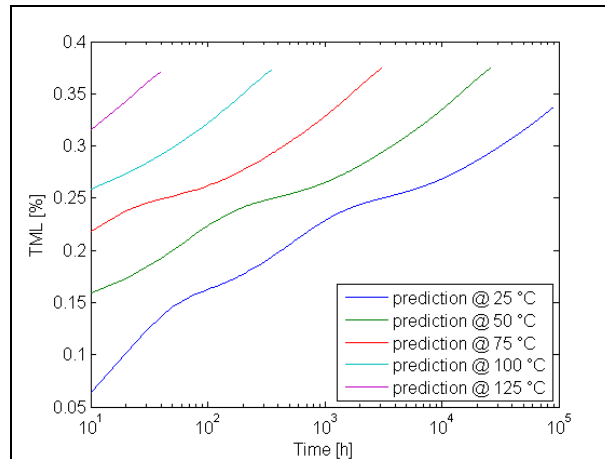
Figure 7-3: Long-term prediction curves

7.3 Ougassing and condensation (methods used during COMOVA development)

7.3.1 Outgassing model in use

Concerning outgassing, the model implemented in COMOVA followed the classical ESTEC approach. Parameter extraction of course had to use the same laws. Outgassing was modelled through the desorption law [4-1]. The temperature dependence of the desorption time constant was simplified wrt the Arrhenius law [4-2] into:

$$\tau_d^\alpha(T) = \tau_{d0}^\alpha e^{-k_d^\alpha(T-T_0)} \qquad [7\text{-}6]$$

with T_0 : reference temperature (K)

        τ_{d0}^α : outgassing time constant at reference temperature (s)

        k_d^α : empirical coefficient for temperature effects (K^{-1})

At constant temperature, this yields an exponential decay of the remaining contaminant:

$$m(t,T) = \sum_\alpha m^\alpha(t,T) = \sum_\alpha m_0^\alpha e^{-t/\left(\tau_{d0}^\alpha \cdot e^{-k_d^\alpha \cdot (T-T_0)}\right)} \qquad [7\text{-}7]$$

with $m(t,T)$: total contaminant mass remaining in/on the material at time t after outgassing at temperature T (g·cm^{-2})

        $m^\alpha(t,T)$: mass of species α remaining in/on the material at time t after outgassing at temperature T (g·cm^{-2})

        m_0^α : initial mass of contaminant species α in/on the material (g·cm^{-2})

Increasing the temperature simply results in a time acceleration by a factor exp($k_d^\alpha \cdot \Delta T$), which may be uniform if all species have the same k_d^α, as it is commonly assumed in practice.

7.3.2 Condensation model in use

Concerning condensation, a sticking coefficient was defined as a function of temperature:

$$S^{\alpha}(T) = \frac{1}{2}\left(1 - \tanh\left(\frac{T - T_C^{\alpha}}{2\Delta T_C^{\alpha}}\right)\right)$$ [7-8]

with T_C^{α} : the captation temperature for species α (K)

ΔT_C^{α} : the transition width for species α (K)

The sticking coefficient $S^{\alpha}(T)$ has a transition from 1 much below T_C^{α} to 0 much above, with a transition width around ΔT_C^{α}.

The deposit on a QCM at temperature T_{QCM} results from [7-7] and [7-8] for outgassing at temperature T (and time accelerated otherwise):

$$m_{deposit}(t,T,T_{QCM}) = \sum_{\alpha} S^{\alpha} \cdot (T_{QCM}) \cdot \left(m_0^{\alpha} - m^{\alpha}(t,T)\right) \cdot F =$$

$$= \sum_{\alpha} S^{\alpha} \cdot (T_{QCM}) \cdot m_0^{\alpha} \cdot \left(1 - e^{-t/\left(\tau_{d0}^{\alpha} \cdot e^{-k_d^{\alpha} \cdot (T - T_0)}\right)}\right) \cdot F$$ [7-9]

with $m_{deposit}(t,T,T_{QCM})$: total contaminant deposit on a QCM at temperature T_{QCM} at time t after outgassing at temperature T (g·cm^{-2})

F : view factor from contaminant source to QCM for source and deposit expressed as fluxes (-)

7.3.3 Parameter extraction

Experimental data available for each material were a TML and usually three CVCMs for three different QCM temperatures, -25 °C, -50 °C and -75 °C.

TML was handled following the classical ESTEC approach (the used parameters were those extracted by the classical method of clause 7.2.2 at the time of the experiments at ESTEC). In brief in this approach the temperature coefficients k_d^{α} are derived from the TML slope changes at the temperature steps (a single common coefficient for all species outgassed by a material). The outgassing time constants at reference temperature, τ_{d0}^{α}, are "manually" determined, and the initial contaminant masses m_0^{α} are determined by a least square fit of the linear combination of functions [7-7].

For CVCM treatment a simplified method was developed to assess sticking coefficients. In a first step they can be considered to be 6 × 3 = 18 unknowns $S^{\alpha}(T_{QCM})$, for 6 species, α = 1 to 6, and 3 QCMs, i = 1 to 3. Since they appear linearly in eq. [7-9] an ordinary least square method could be used for a direct determination. It can however be checked that in practice the spreading of outgassing time constants makes the contributions of each species somewhat disjoint. More precisely in the interval $[\tau_0^{\alpha}/2, \tau_0^{\alpha}]$, almost only the species α is outgassed. This allowed an even simpler method by simply approximating the sticking coefficient of species a as the CVCM to TML ratio during that time interval:

$$S^{\alpha}(T_{QCMi}) \sim \frac{m_{deposit}(\tau_0^{\alpha},T,T_{QCMi}) - m_{deposit}\left(\frac{\tau_0^{\alpha}}{2},T,T_{QCMi}\right)}{\left(m\left(\frac{\tau_0^{\alpha}}{2},T\right) - m(\tau_0^{\alpha},T)\right) \cdot F} \quad [7\text{-}10]$$

where $m_{deposit}(t,T,T_{QCMi})$ is the total contaminant deposit on QCM i at temperature T_{QCMi} at time t after outgassing at temperature T; is indeed the CVCM measured on this QCM

$m(t,T)$ is the total contaminant mass remaining in/on the material at time t after outgassing at temperature T; it has an opposed variation wrt the measured TML

Once, for each species α, the sticking coefficients were known for the 3 QCM temperatures, they only had to be fitted by eq. [7-8] to find the optimal T_C^{α} and ΔT_C^{α}. The basic method consisted in using an asymptotic development of [7-8] for T larger than T_C^{α}, i.e.

$$S^{\alpha}(T) \approx e^{-(T-T_C^{\alpha})/\Delta T_C^{\alpha}} \quad \text{for } T - T_C^{\alpha} >> \Delta T_C^{\alpha} \quad [7\text{-}11]$$

which simplified the fit in a linear regression in logarithmic coordinates. Corrections had eventually to be added since this mathematical fit sometimes led to unrealistic values (T_C^{α} below 0 K or ΔT_C^{α} negative).

7.3.4   Re-emission: a crude approach

In COMOVA re-emission of each species is modelled following first order desorption laws of the type [4-5], with re-emission time constants different from outgassing time constants. However no experimental re-emission data were available at COMOVA development time (late 1990s). A very crude approximation was thus to be made. It was considered that re-emission was faster than outgassing, since outgassing necessarily involves some slowing through diffusion, whether modelled or not. Re-emission time constants were thus simply set so that re-emission at temperature T has the same time constants as outgassing at temperature $T + 50$ K.

7.4   Outgassing, condensation and re-emission (COMPEX, non linear methods)

The physical laws of clauses 4 and 7 all involve simplifications and may be improved. This section does not deal with this kind of physical improvements but of the mathematical methods for deriving the parameters of the physical law from experimental data.

The mathematical methods of clauses 7.1 and 7.3 may all be improved. They are mostly based on linear least square methods and rather crude methods for parameters whose effect is not linear. It results in constraints on the parameters (like having the same k_d^{α} for all species), or probably in sub-optimal values (e.g. for τ_{d0}^{α} or T_C^{α}).

The main idea for improving that consists in taking advantage of the increasing power of computers to use methods suitable for non linear parameters. Typical methods are gradient methods where the

fit of the experimental data is optimised iteratively by progressively modifying the parameters, i.e. moving them in the space of parameters.

A difficulty of such methods is the starting point. If the initial parameter set is too far from its optimal value, the algorithm is usually unable to find the optimum since the gradient to it is not visible. The approximate methods above can be a good way to find reasonable starting values.

Such methods are particularly well suited for extracting parameters with non linear effects (e.g. τ_{d0}^{α} or k_d^{α}, as opposed to m_0^{α}) or for non linear effects (like species mixing effects). They were e.g. recently applied to global outgassing - deposition - re-emission parameter optimisation through COMPEX code (COntamination Model Parameter Extractor).

8
The European modelling tools

8.1   COMOVA

8.1.1   Used equations

COMOVA models contamination deposits and fluxes (and also column densities) in two steps:

*   computation of mass transfer factors in rarefied flow regime taking into account direct view, reflections on surfaces and gas phase collisions. Semi-enclosed cavities can be accurately modelled thanks to a formal summation of processes involving an arbitrary number of reflections,

*   deposits integration over the mission taking into account outgassing, partial sticking and re-emission.

The equations used for the second step in COMOVA are among the ones described above. Outgassing is described by first order desorption law [4-1] and the simplified temperature dependence of time constants [7-6]. Condensation is ruled by the sticking coefficient of eq. [7-8]. Finally re-emission also obeys to a first order law of the type [4-5] with a simplified temperature dependence of time constants of the type [7-6].

8.1.2   Input and output parameters

For each material, the following contamination parameters are needed:

* N number of emitted species (maximum 10)
* h_0 reference thickness (m)
* T_0 reference temperature (°C)

Next, for each emitted species, the input parameters are the ones needed by the equations governing their emission, deposition and possible re-emission (with units sometimes differing from those mentioned above). Concerning outgassing the parameters are the following:

* m_0^α initial mass of contaminant species α in/on the material (% of material mass)

* τ_{d0}^α the outgassing time constant at reference temperature (h)

* k_d^α the empirical coefficient for temperature effects on outgassing (K^{-1})

Concerning the sticking, the input parameters are the following for each species:

* T_C^α the captation temperature for species α (K)

- ΔT_C^α the transition width for species α (K)

and for re-emission:

- $\tau_r^\alpha(T)$ the re-emission time constant of species α (h)

- k_r^α the empirical coefficient for temperature effects on re-emission (K⁻¹)

8.2   SYSTEMA

8.2.1   Overview

The Systema / Outgassing computes deposits and column density induced by material outgassing in space. It consists in a two steps approach:

- Mass transfer factors computation assuming that the flow is rarefied. The computation takes into account direct transport from one surface to another and scattering by the ambient atmosphere (assuming on collision)

- Deposits integration over the mission taking into account the material properties and the temperatures evolution of the surfaces

8.2.2   Used equations

The equations used in Systema / Outgassing are among the ones described above. Outgassing is described by first order desorption law [4-1] and the simplified temperature dependence of time constants [7-6]. Finally desorption also obeys to a first order law of the type [4-5] with a simplified temperature dependence of time constants of the type [7-6].

8.2.3   Input and output parameters

The input parameters are the ones needed by the equations under use. Concerning outgassing each material involves several species. Two similar models: CNES and ESA are used to describe the kinetics of emission and re-emission. The model parameters for the ESA model are:

for each material

- N number of pseudo-species
- h_0 reference thickness (m)
- T_0 reference temperature (K)

for each pseudo-species

for emission:

- m_0^α initial mass of contaminant species α in/on the material (% of material mass)

- τ_{d0}^α the outgassing time constant at reference temperature (h)

- k_d^α the empirical coefficient for temperature effects on outgassing (K⁻¹)

for re-emission:

- $\tau_r^{\alpha}(T)$ the re-emission time constant of species α (h)

- k_r^{α} the empirical coefficient for temperature effects on re-emission (K^{-1})

for scattering:

- $M\alpha$ the molar mass of the species α (g/mol)

- $\Phi\alpha$ the molar diameter of the species α (m)

Output parameters are, as function of time:

- The remaining mass of each outgassing species on each mesh (kg)

- The deposited mass of each outgassing species on each mesh (kg)

- The density of each outgassing species along each point for column density computation (kg/m³)

Annex A
Materials identification card (MIC) - DRD

A.1   DRD identification

A.1.1   Requirement identification and source document

This DRD is called from ECSS-Q-TM-70-52, requirement 5.1.1a.

A.1.2   Purpose and objective

The purpose of this document is to uniquely identify and to provide the properties of the material under testing.

A.2   Expected response

A.2.1   Scope and content

<1>   Description and history of sample

a.   The materials identification card shall contain the following information:

    1.   Trade name and number

    2.   Manufacturer

    3.   Type of product

    4.   Chemical nature

    5.   Processing details.

<2>   Sample batch

a.   The materials identification card shall contain the following information:

    1.   Batch number

    2.   Sample quantity (surface, thickness, total mass + masses of different outgassing components)

    3.   Sample configuration

    4.   Preparation date

    5.   Prepared by.

<3>   Material and substrate

a.   The materials identification card shall contain the following information:

   1.   Material density (total + densitiy of different outgassing components)

   2.   Substrate density

   3.   Substrate material

   4.   Fibre/inert filler information (material, density).

<4>   Miscellaneous

a.   The materials identification card shall contain the following information:

   1.   Contractor/Experimenter (to be filled by the testing laboratory)

   2.   Sample code (according to the project DML)

   3.   Project/cost code

   4.   Originator name and signature

   5.   Application

   6.   Test specification number

   7.   Quality control sample or evaluation sample.

<5>   Outgassing screening data

a.   The materials identification card shall contain the following outgassing screening properties:

   1.   TML

   2.   RML

   3.   CVCM.

<6>   Test reference number

a.   The materials identification card shall contain a test reference number.

A.2.2 Special remarks

An example of a materials identification card for kinetic outgassing test is shown in Figure A-1.

Materials identification card			

Description and history of sample
 	
a. Trade name + number
 	
b. Manufacturer
 	
c. Type of product
 	
d. Chemical nature
 	
e. Processing details:
    e.g.   - joining method
           - heat treatment
           - cure and post-cure
           - additional pre-treatments
           - cleaning method
           - relevant spec. no
	a. Aeroglaze Z306 + Pyrolac P123	b. Lord Corporation / Akzo	

	c. Paint, conductive, black, Primer yellow	d. Polyurethane / Epoxy	

	e. Mix ratio: Primer P123 : Hardener = 100 : 25
	                 Paint S125 : Z306 : MEK = 50 : 100 : 60
	
	   Cure: 24 hours at room temperature + 6 days at 65 °C
	
	   Cleaning with IPA		

Batch number	1108447	Material density (total + density of different outgassing components)	0,95 kg/m^3 (total)
Sample quantity (surface, thickness, total mass + masses of different outgassing components)	A4 sheet, 0,5 mils, 0,74 g (total outgassing mass; estimated from surface and density info)	Substrate density	2,70 kg/m^3 and 0,0432 g/cm2
Sample configuration	1-side outgassing surface	Substrate material	Aluminium foil 16 μm
Preparation date	6/4/2009	Fibre/inert filler information (material, density, etc.)	N/A
Prepared by	Name Surname (Organisation)		
Contractor/Experimenter	Contractor	Project/Cost code	XYZ project
Sample code (refer to the DML item number of the project)	XYZ-CO-LI-0001, issue2.0, item 12.02	Originator name and signature	Originator
Application	Coating optical equipment		
Test specification number	ECSS-Q-TM-70-52A, DOK test method	Quality control sample or evaluation sample	Evaluation
For materials and processes division use Date received: 13/4/2009 Test date: 20/4/2009 Responsible section: TEC-QTETest number: ESTEC 834 Report number: TEC-QTE-4747		micro-VCM test results (acc. to ECSS-Q-ST-70-02C): Reference: TEC-QTE-4707 TML = 1,55 % RML = 0,47 % CVCM = 0,00 %	

Figure A-1: Example of filled MIC (figures in the filled fields are examples only and shall not be considered as reference)