Manuscript Details

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Abstract

The aim of this work is a technical review about Quartz Crystal Microbalance (QCM) sensors used in space missions, i.e. Space Shuttle flights, i.e. NASA Space Transportation System (NASA STS) and satellite missions, that aimed at monitoring the contamination generated by outgassing processes of materials onboard satellites and sensitive payloads. The contamination processes are critical for scientific instrumentation (e.g. optics, telescopes, detectors) because scientific measurements and performances can be jeopardized or worsened by uncontrolled contamination. This issue has been addressed by the space agencies, e.g. NASA, ESA and JAXA that have implemented many different studies to monitor the material outgassing and degradation in space environment. During the past years, the QCM sensors have become the baseline solution for measuring material outgassing and characterizing the on-orbit contamination environment. This work summarizes the main QCM applications in Space and their findings, providing an overview of the sensors' performances in terms of stability, power, data rate, measurement accuracy and resolution. Different QCM technologies will be compared highlighting the advantages of their use for the next space missions and instrumentations that require an accurate monitoring of contamination environment. In particular, due to more severe contamination requirements for next payloads and instrumentations, QCM sensors would be useful to estimate the cleanliness degree by evaluating the induced contamination and degradation on sensitive instrumentations.

Keywords	quartz crystal microbalance; contamination monitoring; molecular and particulate contamination; outgassing; satellite contamination; spacecraft contamination
Manuscript category	Physical Sensors (magnetic, temperature, and others)
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Submission Files Included in this PDF

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18th December 2017

Dear Mr. or Mdm.,

My name is Fabrizio Dirri and I am interested to publish a paper review based on Quartz Crystal Microbalance (QCM) sensors for space applications. I think that it will be useful to know the different space applications (Shuttle flights and satellite missions) and the obtained results which have seen this kind of sensor.

In particular, QCM-based devices were used to monitor the contamination processes generated by outgassing materials onboard the spacecraft that can be dangerous for scientific instrumentation performances, e.g. optics, telescopes. In this way, the National Space Agencies are very interested in the QCM technology, useful to characterize the materials degradation to be used for in-flight mission. For these reasons, specific test procedure (thermal tests in vacuum chamber) are performed each day to study the kinetic outgassing and monitor the outgassing rates of each materials used for the future satellite and spacecraft missions in the ESA, NASA and JAXA facilities.

In the past, QCM devices became the industry's top choice for measuring material outgassing properties data and characterizing the on-orbit contamination environment as well the atomic oxygen erosion which occur for Low Earth Orbit.

The paper review would summarizes the most important QCM applications and the relative performances in terms of stability, power, data rate, accuracy, resolution in particular focusing the attention on the QCM's device configuration and evaluation methods to study the material outgassing processes applied during the Shuttle and satellite missions. A discussion and comparison between QCM devices performances and results are also presented.

I come to you with a PhD in Radar and Remote Sensing, as well the knowledge obtained during my research fellowship: “Thermogravimetry analysis (TGA) by means of Piezoelectric crystal microbalances" and "*Characterization of meteorites and organic materials by means of Spectroscopy Vis-IR and TGA techniques*". At the moment, I’m working for Contamination Assessment Microbalance Project which aims to develop and test a new QCM-based device to monitor the contamination induced from spacecraft materials during in-orbit space missions. I hope that you will look favorably upon my interest to publish this paper review. Thank you for your time, consideration and forthcoming response.

Yours sincerely,

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-Reviewer 1

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General comments

The author greatly improved the English grammar of the manuscript and thus the major concern about this work, as appeared in my first review can be considered no more present.

Some corrections are still to be done inside the manuscript before it can be considered totally ready for the publication.

The great part of these corrections can be considered really minor, but some of them are, on the contrary, of main importance and fundamental for the publication.

Inside these latter I propose to add a brief description of and comparison with other methods to perform measurements similar to those performed by QCM in space and here discussed in order to better point out how QCMs are crucial for this type of applications.

A complete review with particular attention to English language was performed and many sections and sentences were rewritten. All the authors contributed to reorganized the manuscript following the suggestions of both the referees. Basically, the Abstract, Introduction (Sec. 1 and 1.1.), QCM for space applications (Sec. 3) and Conclusions (Sec. 5) were reviewed.

A discussion about different methods able to perform similar measurements performed by QCM was added in Section 1. In particular, these methods were treated by discussing the advantages and disadvantages for each for space and on-ground applications. Modified at Page 1-2-3, line 29-33 and 1-31 and 1-7, respectively.

Major comments

Section 1: Introduction

Table 1: Please condense the first two columns, specifying Polymer/Material inside the column. Where data are not present are they not available or the material does not present outgassing? Please specify in the table (use for example N/A for not available and 0 for a zero value)

This Table (now n.2) was shifted at Page 6, line 8-14 (Sec. 1.1) by following the paper reorganization suggested by the second referee. The columns were condensed into one by specifying the polymer or material. Some data were not available, thus "N/A" format was used where necessary.

Section 2.1: QCMs working principles

Page 7 line 2: please specify what are AT-cut and BT-cut crystals

The two configuration AT-cut and BT-cut crystal were described at page 9, line 30-34:

"AT-cut crystals (that operates in thickness shear mode with crystal's X axis inclined by 35° 15' from Z axis, operating in a wider temperatures range, for frequency range from 0.5 to 200 MHz)"

and

"BT-crystals (that operates in thickness shear mode, too and poorer in temperature stability from AT-cut crystal with a different angle, i.e. 49° from the Z axis)"

Section 2.2: QCM device configurations for space use

Page 7 line 36: QCMs are not "composed of metal foil", but it can be covered by a metal foil (as you describe in Page 8 line 2, talking about the gold coated electrode)

The sentence was corrected at page 10, line 33 as suggested by referee as :

"and coated by metal films (e.g. gold, chrome, platinum)"

Page 10 lines 11-15: I didn't understand why no advantage is provided by the DC configuration in this case. Please explain it better.

In this case, the DC configuration didn't provide advantages due to many frequency spikes caused by direct solar irradiance on TQCMs. Indeed, the fake signal of frequency corresponded to a fake deposited mass on the sensor surface. Basically, due to the frequency spikes of the "sensing crystal" (caused by direct solar illumination) the DC cannot provide the advantages in terms of temperature stability and compensation between the coupled crystals.

The sentence was corrected at page 13, lines 17-19.

Page 9 Figure 1 caption: You didn’t explain the acronym CQCM before its appearance. Please correct.

The acronym was explained at page 12, lines 8-9.

Section 2.3: QCM provider companies

Page 10 line 31: You never explained the acronym TQCM before its appearance here. Please correct.

The acronym was explained at page 14, line 2-3.

Page 11: I would prefer to transform this long bullet list to a table.

A new table was added. Page 14, Table 4.

Page 12 Table 3: Is the address row really needed? We are talking about physical characteristics. I would add, instead, a row with references to works that used the different QCMs in order to support the row “Applications”.

The address row was deleted at Page 15, Table 5. I think that the references to support the row “applications” is not necessary in the table:

- because the row “applications” of QCM used for space missions (provided by QCM Research, CrystalTeck and Meisei) are well described in Sec. 3.1 where all the references are given. By considering the QCM for on-ground applications, the link with the QCM-based products available on the market are listed in the first row of table 3.

Section 2.4: Method ASTM-E1559 standard

General comment: is this section needed in this long form?

This section was reduced (only the methods A and B and their differences were described) as suggested by referee and co-authors. Sec. 1.1, page 4, lines 19-37 and page 5, lines 1-22.

Page 13 line 11: “as an improved version to measure”: this sentence should be used for a standardized procedure (that can be improved). Please rephrase.

The sentence was rephrased at Page 4, lines 27-28 as:

“The ASTM-E1559 standard test method was established in 1993 in order to perform measurements of Total Mass Loss (TML) and Collected Volatile Condensable Materials (CVCM)”

Page 14 lines 1-16: Now I better understood the two methods. However, a better explanation is required for the readers.

The description of the two methods and their differences were improved at Page 5, lines 1-9.

Page 15 lines 9-10: It seems to me that you first put the QCMs at 300 K and the chamber at 75K, but then you are talking about the QCMS passing from 77K to 298K. It's a bit confusing.

The experimental procedure was deleted from the ASTM method description. The experimental procedure it is not crucial for the purpose of the manuscript.

Page 15 line 12: You have always used absolute temperatures (Kelvin), now you write down °C values. Always use the same scale, otherwise the reader is confused.

The experimental procedure was deleted from the ASTM methods description.

Section 3.1: Historical view, missions and experiments

Page 17 line 8: Has the "Russian Agency" a formal name and acronym? Please use them.

The Roscosmos is the Russian Space Agency. Modified at Page 17, line 16.

Section 3.2.1: LDEF (STS-32)

Page 19 line 18: The two types of coating described are for the two QCMs used in DC?

As stated at page 21, lines 1-4, the two pairs of crystals used in DC configuration were coated by In2O3 (the first one) and ZnS (the second one). The first one was functioning during the 424 days of mission whereas the second one (ZnS) was also flown but not monitored.

Page 20 line 2: "The QCM consists of a pair of crystals": this seems incorrect to me. A QCM is made by a crystal. Maybe the experimental setup consisted of a pair of crystals.

In this experiment (LDEF), the QCMs were in DC configuration (two coupled crystals each). In this field, we used to call: "QCM sensor head", the pair of crystals provided by its proximity electronics. In order to avoid misunderstanding, the sentence was modified in Sec. 3.2.1 (page 20, line 18) by using: "QCM sensor head".

Page 21 Figure 3: this figure is at very low resolution. In particular, the legend inside the plots are not readable. If you want to use this figure please describe the difference between solid and dashed lines.

The figure 4 was deleted and reproduced by using the scheme of QCM sensor heads. Page 21, line 9-15.

Section 3.2.3: REFLEX (STS-72)

Page 22 lines 23-25: The four ram angles are first (18°, 20°, 61° and -62°) and then (18°, 19°, 61°, -62°). The second value is different between the two sets. Please always use the correct one.

The angle: 19° was corrected with 20° at Page 24, line 2.

Page 23 lines 1-2: You are talking of an "equation", maybe it would be better to use the term "function". And please add the 3-D plot you are talking about.

The term "function" was used and the 3-D plot was added at Page 24, lines 5-13.

Section 3.2.4 IECM (STS-2,9)

Page 23 line 15: Once again you are talking about "each microbalance consisted in two matched crystals". According to me every crystal is a microbalance. A couple of microbalances are a measurement device in double configuration. If you don't agree please specify why.

Generally, in the technical reports the authors defined: "microbalance", the "QCM sensor head" that is composed by one crystal or two coupled crystals (depending to the configuration, SC or DC) and its Proximity Electronics (PE). In this way, we define a "microbalance" the: crystal/crystals + PE. In order to avoid misunderstanding, the sentence was modified at page 24, line 21.

Section 3.2.5: Hubble Space Telescope (STS-82)

Figure 8 is hardly understandable and linkable to the data descripted in the manuscript.

Because of the poor resolution and description found in literature the image was deleted at page 27.

Section 3.3.1: PIC experiment

Page 26 lines 13-14: "According to the International Space Station (ISS) molecular deposition onto ISS sensitive surfaces": this sentence is very confusing

The phrase was rewritten as: "according to the International Space Station (ISS) external contamination control requirements on sensitive surfaces" at page 27, line 21-22.

Page 26 lines 15-19: the discussion about quiescent and non-quiescent periods is not clear. You first say that the contamination is limited to 130 A/y, then 30 A/y for quiescent periods and finally 100 30 A/y for non-quiescent periods. Maybe the limit is 130, in quiescent periods a normal rate is 30 and in non quiescent 100? Please explain.

Generally, the contamination limits are different depending to the period (quiescent and not-quiescent). The total contamination limit is 130 Å.

The phrase was rearranged at page 27, lines 21-28:

"According to the International Space Station (ISS) external contamination control requirements, the molecular deposition on sensitive surfaces from all contaminant sources is limited to 130 Å per year (Soares and Mikatarian 2003). During "quiescent" period (periods of nominal Space Station operations, which includes materials outgassing and nominal venting) the molecular deposition rate is limited to 10^{-14}

gr/cm^2/sec that translates to approximately 30 Å per year (Soares and Mikatarian 2003). During the "non-quiescent" period (where significant disturbances are introduced to the environment, i.e. Space Shuttle and visiting vehicle proximity operations, ISS reboost and attitude control), the molecular deposition rate is limited to 10^{-6} gr/cm^2/year (that translates to 100 Å per year)."

The total contamination from all the sources will be 130 Angstroms per year.

Section 3.3.2: MEDET experiment

Page 28 lines 17-18: here you expand the acronym MEDET already cited in previous sections. Maybe would be more correct to expand it the first time you cite it.

The acronym MEDET was extended at page 10, lines 14-15 as well as EOIM acronym extended at page 10, line 15.

Page 28 line 33: Substitute "Otherwise" with "On the contrary". As far as I understood you are pointing out that the gold-coated QCM has a variation only linked to temperature, whereas the carbon-coated one is measuring some intrinsic variation.

The sentence was changed. Page 30, line 10.

The aim of the three QCMs were different: the first one was used to monitor the contamination processes, the second one aimed to measure the atomic oxygen erosion by using the carbon coating and the third one was used as reference crystal to monitor the effects on the frequency of temperature fluctuations.

Thus, the QCM2 measured the atomic oxygen erosion (the frequency decreased) during several weeks while the QCM1 frequency variations were mainly linked to temperature fluctuations data recorded by QCM3.

Page 28 lines 35-36: You are now citing Figure 10. I think this part can be moved upward, when you talk about the QCM1-QCM3 data.

The figure 10 (Pages 29-30, line 23) was moved upward where the results about QCM1 and QCM3 were introduced.

Section 3.3.3: Mir Space Station contamination observations

Page 30 line 12: You talk about "solar cycles": what are they? I don't think the 22-year cycle. Please specify

In this case, the Mir solar cycle are specific periods with no time in shadow lasting several days that cause an increase in temperature and material outgassing. The increase in QCM frequency is due to solar irradiance that is going to increase the crystal's temperature. The sentence was modified at page 31, line 11.

Page 31 lines 16-18: Of what "two events" are you talking about? The first one (June 1997) has been already described and justified. The second one (December 1997) no, but could a reason be found for it?

Two main deposition occurred, i.e. on June and December 1997. The deposition on June 1997 was described whereas the deposition on December was due to two mass gain events on TQCMs (at -30 and -10°C). Actually, no reasons were found to correlate the deposition on December 1997 to specific one Mir mission event. Explained at Page 32, lines 13-18:

"The deposition occurring on December 1997 was by far the largest TQCM event recorded in the OPM experiment. The deposition occurred instantaneously (but rose over 28 minutes to its peak) and represented two mass gain events of 380 Å and 250 Å for the -30°C and -10°C TQCMs, respectively. Then, the deposited film re-evaporated almost completely. Attempts to correlate the measured mass gain events with Mir mission events had been ineffective, mainly because of synchronization problems between the OPM clock and Mir mission".

Section 3.4.2: SDS-4

Page 32 lines 4-5: "it can be said that the material deposited on the QCM surface increased when the satellite was in the Sun's shadow and decrease when the QCM is in eclipse": what is a Sun's shadow? Maybe is the opposite, i.e., exposed to the Sun?

This comment is referred to OGO-6 mission. The sentence was modified at Page 33, lines 4-7, because it is true that the contaminants increased when the satellite was exposed to the Sun.

Page 32 line 34: "Thus… ": the value 1 mug/cm2 is the sum of the previously cited 0.7 and 0.3 mum/cm2. As far as I understood these three values belong to different phase mission and this should be only a case. Therefore, you should not use "Thus" (that indicates a consequence).

This comment is referred to SDS-4 mission. The phrase was change with "thus". The 1 μg cm^{-2} is the sum of contaminants, i.e. 0.7 and 0.3 μg cm^{-2}, collected during the two years on-ground operations (tests phase). Page 33, lines 35-36.

Page 33 lines 20-21: I didn't find any previous explanation of "space environment" in contrast to "in-orbit measurements": please provide it here.

This comment is referred to SDS-4 mission. Here we are explaining that the QCM results obtained in SDS-4 are in contrast with those obtained from other missions which used QCMs and where contaminants were collected.

The "space environment" sentence was deleted. Indeed, the SDS-4 was in LEO orbit, thus we can speak about "in-orbit measurements", i.e. the operative phase of QCM measurements on-board satellites in LEO orbits.

The sentence was rearranged at Page 34, lines 22-24.

Minor comments

Abstract

Page 1 line 13: Space missions à space missions (and use space not Space in all the manuscript)

Modified as suggested at page 1, line 12-13.

Page 1 line 14: “that aimed to monitor” à “aimed in monitoring”

The sentence was modified as “that aimed at monitoring” at page 1, line 14.

Page 1 line 18: worsen à worsened

Modified as suggested at page 1, line 17.

Page 1 line 19: National Space Agencies à space agencies (there is no need of capital letters, also in other sections of the manuscript)

The sentence was modified as “the space agencies” at page 1, line 18.

Page 1 line 25: Space Missions à space missions

Modified at page 1, line 24.

Section 1: Introduction

This section was rearranged into sec. 1 and sub-sec. 1.1. Thus, some corrections were performed in the sec. 1.1.

Page 2 line 7: “the past experiments” à “past experiments”

Modified as suggested at page 2, line 7.

Page 2 line 9: “Outgassing phenomenon … is the cause” à “Outgassing phenomena … are the cause”

This sentence was modified: “Outgassing of materials causes contamination that affects many scientific instruments ....” at page 2, line 9.

Page 2 line 12: “how much are instruments …” à “how much instruments …”

This sentence was modified: “By monitoring the contamination process, it is possible to predict the instruments performances reduction…”, at page 2, lines 11-12.

Page 2 lines 13-14: too much “contamination” words repeated. Try to rephrase

The sentence was rephrased at page 2, lines 12-13.

Page 2 line 17: “The species outgassing firstly” à “The first species to outgass”

The sentence was modified: “The most common species constituting the outgas ...”, at page 2, lines 16-17.

Page 2 line 22: “original species” à “original ones”

The sentence was modified as suggested at page 2, line 22.

Page 2 lines 30-31: “testing and modelling and achieve enough confidence” à I didn’t understand the third “and” and the end of the sentence

The “testing and modelling and achieve enough confidence” was deleted and the sentence was rephrased at page 4, line 9-11:

“Due to the different and multiple sources of contamination, monitoring is frequently mandatory to validate on-ground test and to warrant confidence on the performances of the thermal control surfaces and the measurement of many scientific (optical in particular) instruments in space conditions”.

Page 2 line 32: “materials testing” à “material testing” (in the following there also “materials outgassing” and similar; in these cases always use “material” followed by the gerund)

The sentence was modified at page 4, line 12 and rephrased at page 6, line 3:

“The general outgassing requirement for materials.... ”.

Page 3 lines 14-16: please rephrase. Maybe “e.g. for unmanned ones water dump can happen and docking/undocking can influence the induced contamination” (is this the final word “environment” needed?). After “can” always use the infinite (not the third person with the final “s”)

The sentence was rephrased: “Moreover, high contamination has been observed for ISS and Space Shuttle due external materials degradation, maneuvers of service vehicles, re-boost operations, firings of attitude control systems, dumps and EVA (Extra vehicular activity)”, at page 6 lines 18-19 and page 7 line 1.

Page 3 lines 16-18: The sentence, as written now, is confusing. Maybe it could be better in this way: “Degassing from components are expected both during the first phase of a mission and its later phases” and then describe the different cases already specified.

The sentence was modified as: “Degassing from components is expected during both the first phase of a mission (when the spacecraft proceeds from Earth to Space) and successively (when a worse degradation can occur, e.g. due to solar radiation)”, at page 6, lines 15-16.

Page 4 lines 16-18: Please rephrase.

The sentence was rephrased at page 7, line 11-13:

“Considering the spacecraft velocities, its kinetic energy relative to the surface, is approximately 8×10^{-19} J (5eV), the estimated AO flux is approximately 3×10^{14} atom cm^{-2} s^{-1} (Leger et al. 1987)”.

Page 4 line 24: occur à occurs; limit à limits (the subject is “a self-contamination” at line 22)

The phrase was changed: “A self-contamination aboard spacecraft with deposition of molecular films onto surfaces, deriving from outgassing of adhesives, plasticizers, tape, silicon and other polymers always occurs”, at page 7, lines 16-18.

Page 4 lines 24-27: it seems some words are missing here. “the most sensitive surfaces .. ARE solar voltaic…”? Maybe? Otherwise correct in the correct way.

The phrase was rearranged: “The most sensitive spacecraft surfaces subjected to degradation during several years (i.e., ISS) (Arnold and Hall 1988) are the solar panels and the optical solar reflectors and in general the solar reflecting coatings of the radiators surfaces”, at page 7, lines 18-20.

Page 4 line 35: “for THE International Space Station”; “30 years of operationS”

Modified as suggested at page 7, line 28.

Page 5 line 9: maybe is better and “and” instead of the comma between “levels” and “monitoring”? It seem you are listing only 2 uses of the QCMs.

The sentence was modified: “In order to measure expected contamination levels and monitor the outgassing phenomena and AO erosion in the upper terrestrial atmosphere”, at page 8, lines 2-3.

Page 5 line 19: “to support of the” à “to support the”

Modified as suggested at page 8, line 12.

Page 6 line 1: I would add to “used” also “proposed” as you cite and “in-situ investigation of Europa” that is not yet started.

Modified as suggested at Page 8, lines 24-27.

Page 6 line 6: “by specific Laboratory” à maybe “by a specific laboratory” or “by specific laboratories”?

Modified at page 8, line 29.

Page 6 line 9: insert a comma between “resolution” and “highlighting”

Added at page 8, line 32.

Page 6 lines 11-17: substitute “chapter” with “section” (it is a paper, not a book) and at line 12 move the parenthesis soon after “MSX satellite experiment”.

Modified at page 9, lines 2-9.

Section 2.1: QCMs working principles

Page 7 line 8: UP TO hundreds of …

Modified at page 10, line 5.

Section 2.2: QCM device configurations for space use

Page 7 line 35: “AT cut” à “AT-cut”. Maybe here you are describing what AT-cut crystal is: do it at line 2 of the same page.

Modified as suggested at page 10, line 32 and at page 11, line 7.

Page 8 line 10: substitute the “(“ before “as for MEDET” with a comma.

Modified as suggested at page 11, line 27.

Page 8 line 14: “as contamination and the mass of the crystal increases”: I understood the process, but please rephrase the sentence for clarity.

The sentence was rephrased at page 11, lines 28-30.

Page 10 line 6: “the satellite moves in and out from the eclipse”: please try to better describe the situation.

The sentence was rephrased at page 13, lines 10-12.

Section 2.3: QCM provider companies

Page 10 line 23: why “Industrial Companies” with capital letters?

Modified at page 13, line 31.

Page 10 line 29: the comma should be before “whereas” not after

Modified at page 13, line 37.

Page 10 lines 33-35: If you use “as demonstrated by” I would expect that the device “is able to monitor”, not “was used to monitor”

Modified at page 14, line 6.

Page 11 lines 1-2: “the application of the biomedical field …” à maybe “applications to biomedical field…” and “involved the study of” sounds to me not good.

The sentence was modified at page 14, lines 9-10.

Page 12 lines 6-7: I didn’t understand why this sentence has been inserted here. It seems completely off context

The phrase was deleted at page 14.

Page 12 line 9: “QCM supplier”à “QCM suppliers”

Modified at page 14, line 17.

Section 2.4: Method ASTM-E1559 standard

Page 13 lines 4-9: I didn't understand why "(NASA's Space Environment and Effects Program)" is located at the center of the sentence. If it is a reference should be at the end. However all the sentence is too long and confused. Please rephrase.

The sentence was rephrased at page 4, lines 21-24.

Page 13 line 9: "that take into account" à "that takes into account"

Modified at page 4, line 25.

Section 3.1: Historical view, missions and experiments

Page 16 line 3: "performed on many different NASA STS MISSIONS"

Modified at page 16, line 4.

Page 16 line 4: "in order to measure the contamination levels at various locations and to measure": delete the second "to measure"

Modified at page 16, line 5-6.

Page 16 lines 5-6: "NASA's Space Shuttle Program with first QCMs launch was in November 1981" à "The first QCMs launched on NASA's Space Shuttle Program date back to November 1981"

Modified at page 16, line 6-7.

Section 3.2.1: LDEF (STS-32)

Page 20 line 25: Change "cleaner" with "cleanest"

Changed at page 21, line 29.

Section 3.2.2: EOIM-3 (STS-46)

Page 21 lines 13-14: Please rephrase for the sake of clarity.

The sentence was rephrased at page 22, line 14-15.

Section 3.2.3: REFLEX (STS-72)

Page 21 line 25: Change "in" with "on"

Changed at page 22, line 25.

Page 22 line 13: "TQCM was in the sun" à "TQCM was exposed to the Sun"

Modified at page 23, line 16.

Page 22 line 15: "TQCM A frequency showed a decreasing" à "TQCM A frequency decreased"

Modified at page 23, line 18.

Page 22 line 26: “was devoted to correlates” à “was devoted to correlate”

Changed at page 24, line 3.

Section 3.3.1: PIC experiment

Page 26 line 13: I think “arose” is not needed here

Removed at page 27, line 21.

Page 28 line 2: “lower value than” à “a value lower than”

Modified at page 28, line 24.

Section 3.3.3: Mir Space Station contamination observations

Page 29 line 13: “shown” is not correct here. You can use “showed an excess” or “has been shown to exceed”

Modified at page 30, lines 21-22.

Page 29 line 17: the table should be 7, not 6.

Because of a reorganization of sub-sections, the table number is 10. Modified at page 31, line 3.

Page 30 line 12: You talk about “solar cycles”: what are they? I don’t think the 22-year cycle. Please specify

The solar cycles ae referred to Mir space station and are the periods with no time in shadow lasting several days. Specified on page 31, line 10-11.

Page 30 line 19: “the second QCM1”: how many QCM1 are present? In addition, you refer to Astra-II as QCM2 in the table

The “second” word was removed on page 31, line 17.

The QCM were two on Astra-II: QCM1 and QCM2 but the results for QCM2 were reported, only in Table 10 because of abnormal QCM1 behaviour during a solar orbit. Explained at page 31, lines 20-22.

Page 30 lines 21-22: “was maintained AT temperatures above 0°C”

Changed at page 31, lines 19-20.

Page 30 line 25: “Astra-2” à “Astra-II”

Changed at page 30, lines 19 and 23.

Page 30 lines 26-29: I don’t really like the way this sentence has been written. Please rephrase for clarity.

The sentence was rewritten at page 31, lines 24-26, i.e.:

“Thus, the data collected in these periods have been analysed and correlated with solar orbits (the QCM probably was in local shadow simultaneously with the surfaces in its field of view being heated by the Sun).“

Section 3.4.1: OGO-6

Page 31 line 35: “A twice pairs of crystal”: what are you meaning here?

The sentence was modified at page 32, line 31. Four QCMs were flown on OGO-6 mission.

Section 3.4.2: SDS-4

Page 32 line 38: remove “kept”

Removed at page 34, line 2.

Page 33 line 18: “The QCM had been successfully USED FOR monitoring”?

Modified at page 34, line 20.

Section 3.4.5: DS-1

Page 35 line 18: “Because of” à “Since”, “As” or “Because”

The sentence was modified at page 36, lines 23-25: “This was required since very thin coatings (even about few Angstroms) can produce significant variation in thermo-optical properties (solar absorbance and emittance) for materials used in spacecraft thermal control.”

Page 35 line 26: What is a “monolayer”?

A “monolayer” is one single layer of molecule, organic material or contaminant in thickness. In this case, the monolayer was molybdenum. Page 36, lines 31-32.

Page 35 line 32: “confirming that the propellant - molybdenum can travel upstream”: what is the subject of this sentence? Maybe the molybdenum is the part of the propellant that causes the contamination? The maybe “the propellant (i.e., molybdenum)” will be better.

The sentence was changed as suggested at page 37, line 3.

Section 3.4.6: MSX

Page 37 line 14: “the CQCM was heated from 51 to 99K was able to condense”: the second “was” in this sentence is incorrect. Please rephrase.

The sentence was changed at page 38, line 16-17: "During this operation, the CQCM was heated from 51 to 99K providing frequency increase of 450 Hz due to H_2O *condensation (200 Å thickness film)."*

Page 37 line 16: "with a warm-up rate was", change was with of

Modified at page 38, line 18.

Page 37 line 17: "start to decrease at…" à "start to decrease for temperatures larger than…"

The sentence was changed at page 38, line 19-20: "The 200 Å thickness film started decreasing for temperatures larger than 150K and the entire film was removed at 165K, indicating that the matter was H_2O*, coming from multilayer insulator (MLI) (Wood et al. 1998)."*

Page 38 line 24: "FOR the TQCM4…"

Modified at page 39, line 25.

Page 40 line 12: "showed", maybe "showing"?

Modified at page 41, line 12.

Section 4: Summary of QCMs results

Page 40 line 23: "were used in Space Shuttle flights were used in satellite missions…": too many "were", please correct.

The sentence was modified at page 41, line 22: "QCM-based sensors were used in Space Shuttle flights and in satellite mission for the following goals…."

Reviewer 2

It is acknowledged that many of the specific points from the first review have been addressed, and large parts of the paper have been re-written with new information added. However the level of English is still poor, and some of the content is unnecessarily repeated and/or still disorganized. In my opinion, a thorough proof read and additional re-write is required by the team of authors, concentrating especially on language and organization of the information, before a proper technical review can be performed a second time. The subject and technical content can still be worthy of publication.

A complete review with particular attention to English language was performed and many sections and sentences were rewritten.

All the authors contributed to reorganize the manuscript following the suggestions of both the referees.

Basically, the Abstract, Introduction (Sec. 1 and 1.1.), QCM for space applications (Sec. 3) and Conclusions (Sec. 5) were rewritten and reorganized. In detail:

- *the introduction, sec. 1, was reduced in order to avoid repeated contents and by focusing the attention on the main QCM applications, advantages and disadvantages. In particular, as requested by the first referee, in order to clarify how QCMs are crucial for this type of applications, a brief description and comparison with other methods to perform measurements similar to those performed by QCM in space was added (Table 1).*

- *the section 1.1, where the standard methods for outgassing characterization are described, was re-organized and rewritten. The standard method A and B are discussed while the outgassing rates, CVCM and TML data are reported in Table 2. Then, a discussion about the major factors contributing to contamination and the stringent contamination requirements for space missions was added. Finally, a briefly description of QCM uses in space and laboratories is given.*

- *the section 3 was devoted to QCM Space Shuttle flights experiments, QCM experiments on Mir, ISS and satellites. Finally, a complete list of next space missions that may be take advantages from QCM technologies are listed by describing the contamination requirements and the sensitive surface and instrumentations to be monitored.*

- *the sec. 3.2, 3.3 and 3.4 are devoted to QCM experiments on Space Shuttle Flight, ISS - Mir and satellite, respectively. Some QCM experiments were added in table 10 and described for Mir station.*

- *the sec. 4 was reviewed, better describing the QCM results of Space Shuttle flights and the measured contamination (mass loading).*

- *the sec. 5 was completely rewritten by summarizing the QCM advantages for space applications and non-space applications. The QCM improvements obtained during last years and next space mission contamination requirements are described, too.*

A review of Quartz Crystal Microbalances for Space Applications

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Abstract

The aim of this work is a technical review about Quartz Crystal Microbalance (QCM) sensors used in space missions, i.e. Space Shuttle flights, i.e. NASA Space Transportation System (NASA STS) and satellite missions, that aimed at monitoring the contamination generated by outgassing processes of materials onboard satellites and sensitive payloads.

The contamination processes are critical for scientific instrumentation (e.g. optics, telescopes, detectors) because scientific measurements and performances can be jeopardized or worsened by uncontrolled contamination. This issue has been addressed by the space agencies, e.g. NASA, ESA and JAXA that have implemented many different studies to monitor the material outgassing and degradation in space environment. During the past years, the QCM sensors have become the baseline solution for measuring material outgassing and characterizing the on-orbit contamination environment. This work summarizes the main QCM applications in Space and their findings, providing an overview of the sensors' performances in terms of stability, power, data rate, measurement accuracy and resolution. Different QCM technologies will be compared highlighting the advantages of their use for the next space missions and instrumentations that require an accurate monitoring of contamination environment. In particular, due to more severe contamination requirements for next payloads and instrumentations, QCM sensors would be useful to estimate the cleanliness degree by evaluating the induced contamination and degradation on sensitive instrumentations.

Keywords: quartz crystal microbalance; contamination monitoring; molecular and particulate contamination; outgassing; satellite contamination; spacecraft contamination

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1. Introduction

This work provides an overview of QCM sensors for space applications highlighting their capability to monitor the molecular contamination in space conditions. Thanks to their high sensitivity and real-time operation, QCM sensors are garnering attention by space agencies (i.e. NASA, ESA and JAXA), for the monitoring of sensitive surfaces, onboard spacecrafts. This review highlights the advantages and drawbacks in the usage of QCM sensors to monitor outgassing contamination and degradation of materials, summarizing results available from past experiments. The data supports the need of further QCM development but evidence the remarkable potentialities for future usage in space missions.

Outgassing of materials causes contamination that affects many scientific instruments and in general changes the thermo-optical properties of the surfaces on which it condenses upsetting the thermal control systems and modifying the environment around satellites and Space Shuttle missions. By monitoring the contamination process, it is possible to predict the instruments performances reduction. In details, the two main categories of contamination are the particulate and molecular one.

The molecular contamination occurs mainly because of outgassing of organic materials and even inorganic materials (e.g. ceramics or small electronics components that can trap organics during their processing) and can be considered as a surface evaporation combined with a diffusion for bulk contaminant species. The most common species constituting the outgas (due to processes, test, storage, handling, pre-launch and launch etc.) are water, and organic components: solvents, additives, lubricants, deriving from ground contamination or due to manufacturing processes, test, storage, handling. Moreover, products may derive from material decomposition generated by the exposure of materials to space weather, in particular UV radiation, electromagnetic and charged particles, electrical discharges and arcing, creating molecular species with higher volatility than the original ones (Sørensen 2010).

On the other hand, the particulate contamination is due to particles originating from manufacturing (machining, sawing) or wear (friction), degradation of binder under different environments (e.g. UV), crack formation and subsequent flaking as a result of thermal cycling. Dust particles can be present as well, deriving from atmospheric fall-out (dust) during assembly, integration and storage or deriving from human sources during such activities (hair, fibres from garments, etc.). In the same category, we can find particles produced by spacecraft propulsion, from micrometeoroid or microdebris impacts (Sørensen 2010).

There is a variety of measuring techniques applicable to assess the surfaces molecular contamination. The best method in a specific application depends to the level of cleanliness requirements and other general factors such as cost and schedule. The methods are compared in Table 1 and a brief discussion is given below.

Table 1. (from Tribble et al., 1996). Molecular contamination monitoring options.

Method	Sensitivity (mg cm^{-2})	Advantages	Disadvantages	Application
Gravimetric	0.002	Generally Accepted	24 hr Turn around, handling errors, low sensitivity	Ground processing only
OSEE	0.001	Fast Response	Requires calibration; low sensitivity on some surfaces	Ground processing only

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QCM	5×10^{-6}	Real-Time; High Sensitivity	Only measures mass deposition and characterization of pure compounds	Ground processing and On-orbit
Calorimetry	1×10^{-5}	Real-Time	Only measures absorptance changes	On-orbit only

1. The Gravimetric procedure is used to evaluate the amount of molecular contamination, Non-Volatile-Residue (NVR) on a surface. The procedure is based on ASTM E 1234, ASTM E 1235: the surface is cleaned by using a solvent and the NVR is extracted from the wipers with additional solvent which is evaporated in a vacuum oven or in a Class 100 unidirectional air-flow hood (the mass of residue minus the mass of blank sample, divided the area wiped, gives the mass per unit area of NVR of cleaned surface). This method is well characterized and is considered as a standard for ground processing whereas the disadvantage is that does not provide real-time answer and it is unsuitable for use on optics and other easily damaged surfaces (Tribble et al. 1996) (not adaptable for on-orbit measurements).
2. The Optically Stimulated Electron Emission (OSEE) is based on the measurement of the electrons emission through photoelectric effect by a specific metallic surface subjected to UV light. Actually, if the surface is contaminated, the contaminant layer will absorb some fraction of incident UV and reduce the strength of UV that reaches the metallic surface, i.e. the number of photoelectrons will be reduced. In this case, if the instrumentation is well calibrated, the NVR levels can be inferred. This method does not require a contact with a surface (that makes it suitable for optical devices) and provides real-time data. The disadvantage is that the instrumentation has to be calibrated for a specific surface (because of the variability in the data response) and cannot be used on all surfaces (Tribble et al. 1996). Like the gravimetric method, this method is suitable for on-ground applications only.
3. The calorimetric method is able to measure the degradation of thermal control materials by using the calorimeter instrument. The absorbance coefficient (proportional to contaminant layer thickness) can be inferred from the ratio between the absorbance and emittance coefficients of a specific sample that is derived from the change in temperature of that sample once illuminated. In pre-flight calibration, a sensitive design can be able to infer changes in absorbance as low as 0.0005. Thus, the calorimeters can give information about the absorbance nature of contaminant but cannot provide directly the information about the deposited mass (Tribble et al. 1996).
4. the QCM is able to measure directly the deposited mass of contaminants. The natural frequency of the crystal will change if a mass is deposited on its surface therefore, the mass can be inferred from the change in resonant frequency. The sensitivity depends on the crystal oscillating frequency and is for instance 4.4×10^{-9} g/cm^2/Hz for a 10 MHz crystal (at 25°C). The QCM devices are foreseen for outgassing measurement in the ASTM-E-1559 standard, the procedure coded to test the materials outgassing in laboratory. QCM exhibit many advantages with respect to the other instruments: their temperature can be controlled, they are quite small, light and reliable. By controlling the QCM temperature (TQCM is the temperature controlled device), the mass deposition as a function of surface

temperature can be determined and by associating the condensation temperatures of the different contaminants, in principle an analysis of the composition can be performed. Recently, QCM capability to identify the characteristics of pure organic compounds in relevant environment has been demonstrated by Dirri et al. (2016) while the effectiveness in characterizing mixtures in space conditions is still under investigation.

Due to the different and multiple sources of contamination, monitoring is frequently mandatory to validate on-ground test and to warrant confidence on the performances of the thermal control surfaces and the measurement of many scientific (optical in particular) instruments in space conditions. This explains the growing interest of the space agencies (e.g. NASA, ESA and JAXA), to perform material testing for the characterization of the outgassing properties. Outgassing quality is generally expressed by the combination of three parameters: the Total Mass Loss (TML), the Collected Volatiles Condensable Materials (CVCM) and the Recovered Mass Loss (RML). The measurement of the above parameters is performed according to well-established standards, the ASTM-E1559 (NASA) and ECSS-Q-TM-70-52A (ESA); both of them are based on QCM measurement for the assessment of the CVCM.

1.1. Standard methods for outgassing characterization and space missions contamination requirements

NASA and ESA worked together to create a *Satellite Contamination and Materials Outgassing Knowledgebase* (that includes the TML and CVCM of materials) by using the ASTM Standard E-1559 Method (NASA) (Garrett et al. 1994, Wood 2007) and ECSS-Q-TM-70-52A: Kinetic outgassing of materials for space by using QCMs (http://ecss.nl/hbstms/ecss-q-tm-70-52a-kinetic-outgassing-of-materials-for-space/). The standard method procedure (that takes into account the QCM devices for on-ground uses) for materials selection for space missions is hereafter briefly summarized.

The ASTM-E1559 standard test method was established in 1993 in order to perform measurements of Total Mass Loss (TML) and Collected Volatile Condensable Materials (CVCM) of materials which can be determined by weighting the material samples before and after a heating cycle at 398K for 24 hours in vacuum chamber. The TML is obtained by dividing the loss in mass by the original mass of the sample. ASTM-E1559 is based on QCM collection method that allow to have TML by using 3 or 4 QCMs with two types of test method constraints where the QCMs are cooled to different temperatures (Fig.1) (Garrett et al. 1994, Wood 1997). In order to determine the outgassing kinetics, two methods are used: standard method A and standard method B. Standard method A uses standard effusion cell (a cylindrical container, machined from copper or aluminum of approximately 65±5 mm in diameter by 50±5 mm in depth) temperatures and three QCMs (sensitivity 10^{-8} gr cm^{-2} Hz^{-1} at 298K with a natural frequency of 10-15 MHz) with polished aluminum electrode at standard temperatures. This method provides the apparatus and geometries able to have standard view factors from the QCM to effusion cell orifice. Standard method A requires specific QCMs (three QCM at 90, 160 and 298K while one more QCM at different temperature can be used) and sample temperatures (three for each material sample). Thus, the effusion cell is typically set to 298K, 348K, 323K or 373K depending to the deposition on ≤90K QCM during the previous two tests.

Standard method B method could be also used for outgassing tests and allows for variances of these parameters (temperature set point and number of QCM) by allowing the user to customize tests by using a different parameters or apparatus (setup geometry). Except for effusion cell and QCM-set point temperatures, the actual test temperature is the same for Test Method A or B. One optional QCM provided by gold electrode and coupled with mass spectrometer can be used for Test Method B.

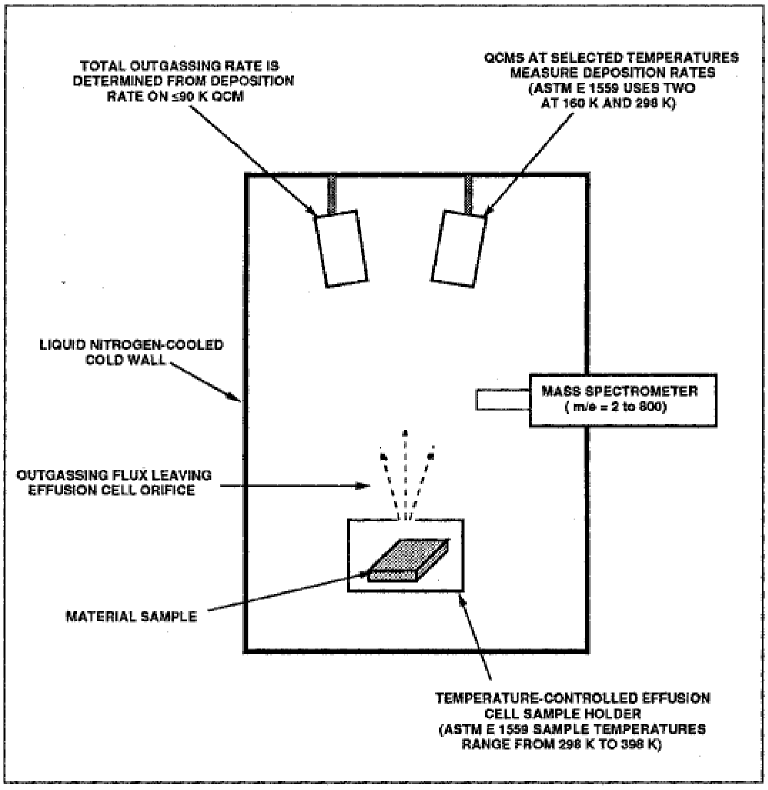

Figure 1. (from Garrett et al. 1994, Wood 2007) ASTM-E1559 setup experiment for outgassing measurements using QCMs sensor [This figure is taken from NASA N45-14066, “ASTM E 1559 method for measuring material outgassing/deposition kinetics has application to aerospace, electronics, and semiconductor industries”, Garrett J.W., Glassford A.P.M., Steakley J.M. and used with permission of NASA].

The information about the various species collected by using standard methods will be obtained by means of ThermoGravimetric Analysis (TGA) cycles as well as the deposition and evaporation temperature of each species. Finally, the material sample is removed from the effusion cell and weighted. The value obtained is compared with the initial value measured at the start of the outgassing test determining the TML and comparing the results with determined deposition values from QCMs sensors.

Table 2 reports the outgassing rates, the TML and CVCM of different polymers and materials commonly used in space (Patrick 1973, Peacock 1980, Anwar et al. 2015, Davis et al. 2013 and *NASA Outgassing Database*

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for Tested Materials). The general outgassing requirement for materials to be used in space is TML<1.0% and CVCM<0.1 % (https://outgassing.nasa.gov/og_desc.html and ECSS Q 70-71A, "Data for selection of space materials and processes"), more stringent levels, typically one order of magnitude lower, are stated for applications on contamination sensitive instruments.

Table 2. Polymers and materials outgassing characteristics, testing results in space conditions (vacuum and high temperatures). Data from 1. Peacock et al. (1980) where the outgassing rates of unbaked and baked polymers in torr l s^{-1} are given and from 2. Patrick et al. (1973) where the outgassing rates of some materials used in space instrumentations (e.g. stainless steel, aluminum alloy, etc.) were reported. TML and CVCM data are also reported for selected materials (3. *NASA Outgassing Database for Tested Materials,* 4. Anwar et al. 2015 and 5. Davis et al. 2013).

Polymer/Material	**Outgassing rate after 1-hour pumping (torr l s^{-1})**	**Outgassing rate after 4-hour pumping (torr l s^{-1} cm^2)**	**Total Mass Loss or TML (%)**	**Collected Volatiles Condensable Materials or CVCM (%)**
Fluoroelastomer^{1,3} (*polymer*)	4×10^{-7} - 2×10^{-5}	N/A	from 0.14 to 0.51	0.00
Neoprene^{1,3} (*polymer*)	5×10^{-5} - 3×10^{-4}	N/A	9.04	0.85
Polyurethane^{1,3} (*polymer*)	5×10^{-7}	N/A	from 0.92 to 9.29	from 0.03 to 0.35
Silicone^{1,3} (*polymer*)	3×10^{-6} - 2×10^{-5}	N/A	from 0.07 to 4.35	from 0 to 1.16
Teflon^{1,2} (*polymer*)	2×10^{-8} - 4×10^{-6}	1.5×10^{-7}	from 0 to 0.52	from 0 to 0.08
PCTFE^{1,3} (*polymer*)	4×10^{-8}	N/A	0.01	0.00
Polyimide^{1,4} (*polymer*)	8×10^{-7}	N/A	from 0.86 to 3.38	from 0.05 to 1.39
Stainless steel^{2,5} (*material*)	N/A	0.05×10^{-7}	0.00	0.00
Aluminium alloy^{2,3} (*material*)	N/A	0.6×10^{-7}	0.05	0.00
Magnesium alloy^{2} (*material*)	N/A	10^{-7}	N/A	N/A
Fluorocarbon rubber^{2,3} (*material*)	N/A	2.3×10^{-7}	0.13	0.00
Mylar film^{2,3} (*material*)	N/A	4×10^{-7}	from 0.07 to 1.65	from 0 to 0.42
Epoxy tape^{2} (*materials*) • CF/Epoxy^{4} • CF/Epoxy^{4} • Kevlar/Epoxy^{4}	N/A	12.5×10^{-7}	from 0.6 to 1.2 from 1.07 to 3.50 from 1.86 to 1.92	from 0.1 to 8.83 from 0.00 to 0.61 from 1.26 to 1.32
Nylon film^{2,3} (*material*)	N/A	60×10^{-7}	from 0.02 to 5.64	from 0.01 to 0.24

Degassing from components is expected during both the first phase of a mission (when the spacecraft proceeds from Earth to Space) and successively (when a worse degradation can occur, e.g. due to solar radiation). High contamination levels are recorded during the on-ground tests and in the first hours in orbit (e.g. during SDS-4 satellite, Nakamura et al. 2013). Moreover, high contamination has been observed for ISS and Space Shuttle due external materials degradation, maneuvers of service vehicles, re-boost operations, firings of attitude control systems, dumps and EVA (Extra vehicular activity) (Green 2001). In addition, thruster firings and the solar effect complicate the contamination detection and data processing from instruments on ground while, at

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altitudes beyond the magnetosphere, the ionization of the contaminate flux performed by solar plasma can reinforce the contaminant by mutual attraction processes (McKeown, 1998).

Although it is not the major factor contributing to contamination, an important source of surface erosions (in the Low Earth Orbit, i.e. LEO environment) is Atomic Oxygen (AO), a strong oxidizing agent, that can causes damages on spacecraft surfaces and oxidation of sensitive material increasing the particles release. The AO major effect is erosion of surfaces that is assumed to result from oxidative attack of the organic polymer chains, producing volatile species and resulting in mass loss (Leger et al. 1987). Thus, the surfaces of orbiting spacecraft can be exposed to a flux of Earth ambient atmospheric species which can cause damages depending on the spacecraft velocity through the atmosphere. Considering the spacecraft velocities, its kinetic energy relative to the surface, is approximately 8×10^{-19} J (5eV), the estimated AO flux is approximately 3×10^{14} atom cm^{-2} s^{-1} (Leger et al. 1987). As observed for Space Shuttle flights (Leger 1982, Leger 1983, Peters 1983), the external organic surfaces are expected to be affected by oxidization process caused by AO. The major effect is recession of surfaces exposed to ram conditions (the side of the spacecraft that points in the direction of the satellite's motion that impacting/ramming into the fluid that the satellite move through). A self-contamination aboard spacecraft with deposition of molecular films onto surfaces, deriving from outgassing of adhesives, plasticizers, tape, silicon and other polymers always occurs. The most sensitive spacecraft surfaces subjected to degradation during several years (i.e., ISS) (Arnold and Hall 1988) are the solar panels and the optical solar reflectors and in general the solar reflecting coatings of the radiators surfaces.

The main identified system issues related to contamination are: 1. degradation of optical surfaces; 2. dropping in the electrical potential of charged surfaces; 3. drift of conductive materials, including residual vapor deposited, from eroded polymer films and minute particles from mechanical galling; 4. decreasing performance of thermal control surfaces; (IR emittance and solar absorptance increase) 5. degrading solar cell performance due to contamination induced loss of transmittance through cover glasses; 6. introduction of particles on mechanical surfaces which may initiate subsequent galling (Levine 1992).

Because of these issues, the contamination requirements for space missions are very stringent. In particular, for the International Space Station (ISS), NASA proposed 30 years of operations although the contamination processes could potentially change the time range considered. For telescope optics, e.g. Herschel, X-ray Multi Mirror mission or XMM, etc. specific contamination limits were defined due to sensitive part of the instruments (Table 3). The range of measurable deposited mass due to contaminants spans from ng cm^{-2} to hundreds of μg cm^{-2}. This large range fully includes the molecular cleanliness requirements of many scientific payloads, such as the XMM optics (200 μg cm^{-2}) (de Chambure 1997), the SPICA telescope (200 μg cm^{-2}) or Herschel telescope (4 μg cm^{-2}).

Table 3. The Space Station and spacecraft contamination limits (Wood et al. 1996, Wood et a. 2000, Bryson et al. 1992, SRE-F/2013.033 ESA-ESTEC 2013).

Spacecraft/satellites	**Instrument**	**Contamination limit (μg cm^{-2})**
ISS	Solar panel, reflectors	0.9 per day
Mir	Hardware component	0.9 per day

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XMM	Optics	200
SPICA	Telescope	200
Herschel	Telescope	4000

In order to measure expected contamination levels and monitor the outgassing phenomena and AO erosion in the upper terrestrial atmosphere, Quartz Crystal Microbalance devices have been chosen in many flight experiments, thanks to their performance, simple working principle and low mass budget. Thus, QCM sensors can be applied to monitor:

- Molecular contamination (e.g. water, solvents, additives, lubricants and decomposition products)
- Particulate contamination (from manufacturing, degradation, UV, thermal cycles etc.)
- Atomic Oxygen flux and erosion (when they are coated with a sacrificial layer, e.g. carbon)

QCMs have been tested either in laboratories (Palomba et al. 2002, Freedman et al. 2008, Dirri et al. 2016), on spacecraft and satellite (for on-orbit measurements of contaminations level), in various Space Shuttle mission (STS) and missions for technologies demonstration in space (MSX, i.e. Midcourse Space Experiment). The first QCMs (gold-coated) flew on the Discoverer 26 Satellite (launched on 26 July, 1961) to support the Atlas Missile program, by measuring the erosion rate of gold films in space. After that mission, other three Discoverer flights measured the sputtering erosion rates of surfaces by 10eV molecular impacts in the upper atmosphere by means of QCMs. Some years later, microbalances were selected to measure contamination in space on the Orbiting Geophysical Observatory (OGO-6), mission launched on June 5, 1969. OGO-6 was a large observatory provided by 26 experiments (e.g. Gas-Surface Experiment, Ion Density Experiment, etc.) designed to study the interrelationships between atmospheric parameters during a period of increased solar activity. The payload held four QCMs to support over a one-year period the Gas-Surface Experiment, measuring 4 μg cm^{-2} during the first ten days after launch (McKeown 1998) while the Ion Density Experiment failed because of high voltage discharge attributed to high contamination cloud enveloping the satellite (McKeown 1998). The lesson learned from the OGO-6 flight, introduced NASA to the contamination issues affecting the operation of the spacecraft which, before the OGO-6 launch was not considered a problem for long-term operation on spacecraft and satellites. Then QCM-based sensors have been more extensively used aboard satellites and spacecraft by the main space agencies (NASA, ESA and JAXA) to support the compounds discrimination (volatiles and refractory molecules) by using TGA heating cycles and proposed for in-situ investigation of Europa (Gowen 2011).

It has to be noticed that all the QCMs currently available for space missions are provided by one US company, i.e. QCM Research Company or by specific laboratories (as Faraday Labs), the monopoly being mainly justified by the gained flight heritage.

Hereafter, QCM sensors and space applications are described more in detail focusing on obtained performances in terms of stability, power, data rate, accuracy, resolution, highlighting how this technology could provide the monitoring of the contamination environment for the next space missions but also the issues found and the technological developments that would be desirable. QCM working principle, drawbacks and their application in outgassing testing method are presented in section 2 whereas, comparison between flight QCMs is provided in section 3. MSX satellite experiment (the first space technology satellite of the Ballistic Missile Defense Organization) has been described in depth due to large arguments discussed of each criticality of this experiment (starting to the solar pulses on QCMs surfaces). The main results obtained in the Space Shuttle flights and satellite missions are discussed in section 4 while an overview of next space missions (with onboard sensitive surface, i.e. optics, detectors, telescope, mirrors etc.) that can take advantages from QCM-technology for in space contamination control and on-ground tests is discussed in section 5.

2 QCMs backgrounds

2.1 QCMs working principle

Quartz crystal piezoelectricity was discovered in 1880 by Jacques and Pierre Curie: when a mechanical stress is applied to certain materials such as quartz, an electric polarization proportional to the applied stress is produced (McKeown 1998). In the late 1950's the resonating quartz crystal was precisely modelled by Sauerbrey (1959) who described the quartz crystal resonator as a quantitative mass measuring device. He coined the term Quartz Crystal Microbalance (QCM) in late 1950's, and his analysis paved the way to the use of quartz plate resonators as sensitive microbalances for thin films. The Sauerbrey equation states that a surface mass density deposition Δm, determines a frequency variation according to the following linear relationship (Sauerbrey 1959):

$$\Delta f = -\frac{f^2 \Delta m}{N\rho} \qquad (1)$$

where ρ is the density of the piezoelectric material (in the quartz case is 2.65 g cm^{-3}) and N is the frequency constant of the specific crystal cut. Furthermore, the QCM sensitivity is given by:

$$\frac{\Delta m}{|\Delta f|} = \frac{N\rho}{f^2} \qquad (2)$$

This means that the mass sensitivity is independent from the physical properties of the deposited material. Since the frequency constant (N) of specific crystal-cut is 1.67×10^5 Hz cm for AT-cut crystals (N_{AT}, that operates in thickness shear mode with crystal's X axis inclined by 35° 15' from Z axis, for frequency range from 0.5 to 200 MHz) and 2.5×10^5 Hz cm for BT-crystals (N_{BT}, that operates in thickness shear mode too but poorer in temperature stability than AT-cut crystal with a different angle, i.e. 49° from the Z axis). The use of AT-cut crystals in microbalances allows obtaining a higher mass sensitivity. The Sauerbrey equation, which implies a linear transduction factor between the measured frequency and the added mass, is valid under in the following hypotheses:

- the film is rigidly coupled to the oscillatory motion of the crystal surface (up to a thickness depending of density of deposited material) (Esmeryan et al. 2013, Vogt et al. 2004);
- limited mass loadings (up to hundreds of μg cm^{-2}).

The first condition is fully met within the application of interest, i.e. the contamination from degassing in space, where degassed species are collected by the cold surface of the quartz crystal. Fulfillment of the second requirement is difficult to predict. Sauerbrey (1959) found that the experimentally obtained mass sensitivity (for an AT-cut 14MHz quartz crystal) was accurate to within the 2% for a deposited mass of up to $\Delta f/f < 0.1$ %.

The theoretical treatment of thin film deposition and the oscillation behavior on a quartz crystal was improved by Stockbridge (1966), who used a perturbation analysis based on a one-dimensional mechanical vibrating system (Rayleigh 1945), but the results converge to the Sauerbrey equation for small amounts of loaded materials (Lu and Czanderna 1984). In particular, as done in different space missions (e.g. MEDET: Materials Exposure and Degradation ExperimenT, EOIM-3: Evaluation of Oxygen Interaction with Materials Experiment-3), the QCMs can be covered with an additional layer in order to control the interaction between two different molecular species (e.g. Carbon/Al_2O_3 and Atomic Oxygen). Following the Sauerbrey relation, the mass of the additional layer decreases the crystal natural frequency. Successively, the species interaction lead to a decrease of the crystal frequency (e.g. carbon and AO) as occurred in the MEDET experiment (Inguimbert et al. 2008). By considering the QCM sensitivity and the minimum measurable frequency, the minimum measurable mass corresponds to 1.6 ng cm^{-2}. The contamination requirement for critical surfaces, e.g. optics, telescopes and spectrometers is in the range 2×10^{-7} - 4×10^{-6} g cm^{-2} (ESA doc., SRE-F/2013.033), QCM sensors therefore, can provide an accurate molecular contamination monitoring for the most demanding space application.

2.2 QCM device configurations for space use

Quartz Crystal Microbalance (or TSMR: Thickness Shear Mode Resonator, 0.8 - 40 MHz) was the first piezoelectric device used to monitor chemical reaction processes in biomedical and industries, absorption/desorption processes and materials corrosion, by taking advantage of piezoelectric effect and exploitig the different SiO_2 cut. Piezoelectric crystals can be manufactured in different way at different frequencies and assembled in different shapes to achieve different vibration modes (e.g. radius vibration, area vibration, thickness shear mode vibration etc.). QCM sensors are mostly made by AT-cut quartz plate (the material deformation act as scrolling of parallel planes) and coated by metal films (e.g. gold, chrome, platinum) whose goal is to generate the acoustic wave through the electrodes polarization (Leger L. 1987, de Chambure et al. 1997). The sensitive region, i.e. the electrode (e.g. gold coated) is usually placed at the center of the crystal that shows high efficiency in capturing chemical and organic materials. The resonance frequency of the QCM sensor is determined by the thickness of the quartz crystal. The thinner the quartz crystal, the higher the frequency resonance.

The QCM resonance frequency is very stable in time and also exposition to UV or even more energetic radiations have small effects but, it depends on the crystal temperature. The temperature affects all the crystal physical parameters on which the natural frequency depends: it changes the thickness through thermal expansion but it changes also the elastic moduli and the density; the combined effect is rather complex and strongly dependent on the angle of cut because of the quartz crystal anisotropy. The usage of AT-cut quartz crystals leads to a minimum of temperature sensitivity for an operating temperature around the 20 °C; that is one of the main reasons for the common adoption of this configuration in ground applications. Nevertheless, when the operational temperature range must be wider than that of the laboratory conditions, the temperature sensitivity becomes an issue and often QCM are made with two crystals to use one as temperature compensator: this is the so called Double Cristal (DC) configuration.

The DC configuration theoretically allows compensating the influence of any environmental factor, beside temperature e.g. pressure or, any drift or aging effect common to similar crystals (Lu an Czanderna, 1984). In the DC configuration, two quartz crystals are selected, typically from the same production batch, with resonance frequencies differing by no more than 1-2 kHz. The two are mounted in a sandwich-like configuration: one crystal is protected from contamination and operates as "reference crystal" while the other one is exposed to the external environment and it is called the "sensing crystal". When the two crystals are at the same temperature they exhibit similar frequency changes whatever temperature. Thus, the measurement of the beating frequency of the two provides compensation of the temperature (or pressure, drift...) effects on the measured quantity. The real case is different because first of all even two close crystals in general are at slightly different temperatures because of different heat fluxes on the external surfaces of the sandwich and even crystals from the same batch in general have slightly different temperature sensitivity.

QCM devices for space missions are built in a Single Crystal (SC) or Double Crystals (DC) configurations whose relative scientific and technological purposes are described as following:

- the SC configuration is simpler and can be often arranged, to reach different goals, in arrays of three or four QCMs, e.g. to monitor the AO, the temperature trend and contaminants, as for MEDET experiment (Inguimbert et al. 2008). In this case, the oscillation frequency changes in relation to the changing mass and temperature of the crystals. In MEDET experiment, when the contamination flux was observed, the oscillation frequency decreased because of the deposited mass on the crystal surface. This kind of configuration can be also used to measure the AO flux with an appropriate coating (e.g. carbon coated); in this case the oscillation frequency increases as the atomic oxygen erodes away the carbon layer and the mass of the crystal decreases Therefore, a separate crystal can be also used to independently monitor the crystal temperature, so that the mass data can be corrected for temperature effects (Inguimbert et al. 2008).
- The DC configuration is more demanding in terms of resources and is mostly used when a single QCM is operated in a large temperature range.

The latter configuration has been selected by many Companies and Laboratories for Space Sensors development, among them the main ones, QCM Research and Faraday Labs whose QCMs have been flown in many satellite and space missions. In Fig.2, SC and DC configurations from MEDET and MSX missions are shown.

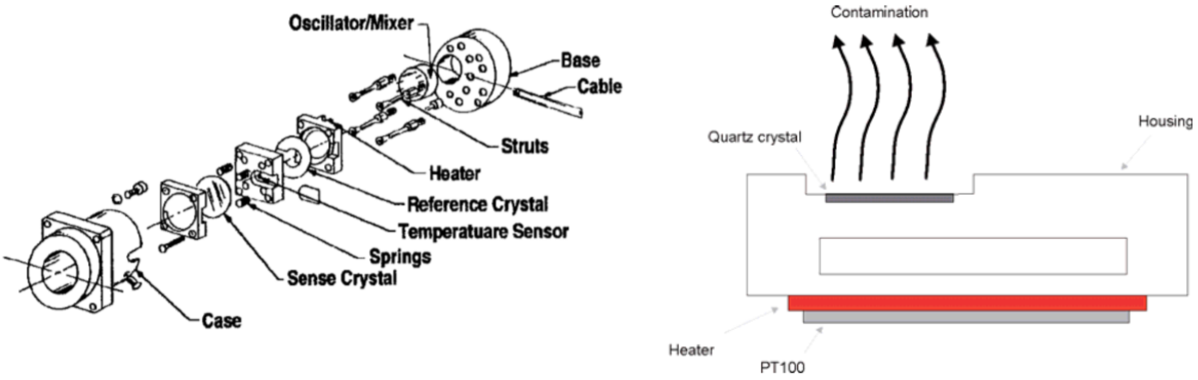

Figure 2. (from Wood et al. 1997, Inguimbert et al. 2008). QCM device configurations. *Left*: The CQCMs (Cryogenic Quartz Crystal Microbalance) is a Mark 16 (double crystal configuration) which was designed and manufactured by QCM Research of Laguna Beach, CA. The CQCM uses two quartz crystals (to minimize temperature effects). *Right*: QCM system (single crystal configuration, in heating mode) used in MEDET experiment (ESA) onboard ISS.

The difference between the two configurations (SC and DC) with respect to the temperature effect is clearly shown in Fig.3 which provides two measurements in a thermo-vacuum chamber obtained by using a DC sensor, i.e. MK 20 by QCM Research (Palomba 2001) and the SC Volatile In-Situ Thermogravimeter Analyser (VISTA) breadboard developed for the Marco Polo mission equipped with a single quartz crystal (Palomba et al. 2015). In both cases, no mass deposition was present. The different temperature sensitivity of the two systems is evident: a much larger frequency variation is shown by the SC configuration, with a temperature variation of about 70°C than by the DC one with 100 °C change.

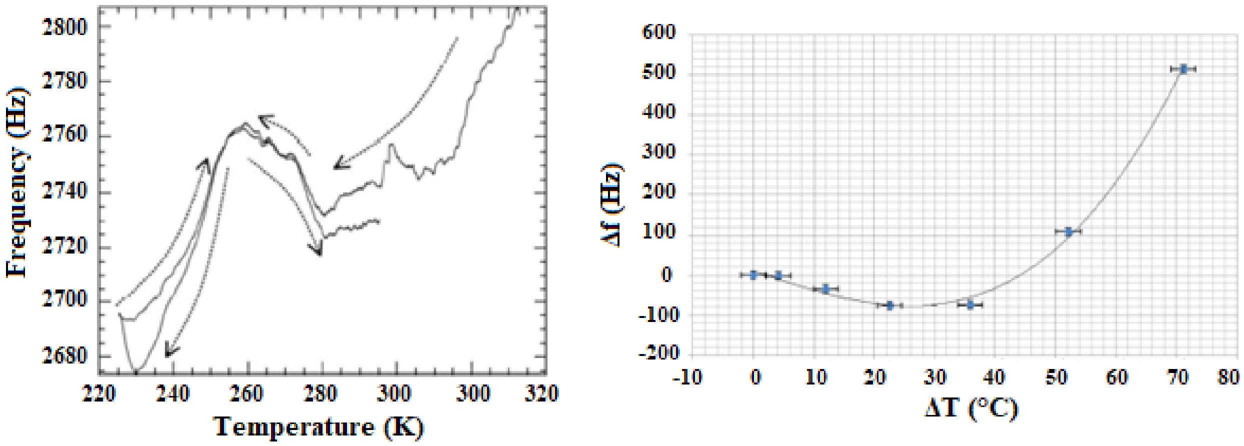

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Figure 3. QCM frequency as function of its temperature. *Left*: the beating frequency behavior, relative to the commercial MK20 DC is shown. Between 220 K and 340 K the frequency increases of about 120 Hz (Palomba et al. 2001). *Right*: the frequency of the Volatile In-Situ Thermogravimeter Analyser (VISTA), where the frequency variation is as high as 600 Hz for a ΔT~70°C (VISTA IDR-Marco Polo 2009).

However, the environmental conditions related to space mission scenarios have an important role on the QCM performance in terms of temperature and frequency stability. Different operating environments can be identified, e.g. for deep space missions the QCM would work mainly at cryogenic temperature whereas for LEO orbit (e.g. REFLEX, HST, PIC etc.), wide thermal cycles will be likely to occur. Thus, during LEO orbits the temperature in operation can change even abruptly and several thermal cycles can be induced on QCM sensors typically at each eclipse pass. In fact, if solar illumination reaches the sensing area of the crystal, the result is a sudden temperature increase that will generate spikes on the recorded frequency both for SC or DC configurations, as for MSX experiment. This effect can create inaccuracies in the data analysis on a short term basis. As an example, frequency changes as large as 450 Hz were measured with the Sun going on-off with respect to the QCM field of view (Wood et al. 1998); this corresponded to fake mass loading of 882 ng cm^{-2} (for a QCM frequency of 15MHz). In this specific case, the DC configuration would not offer better performance with respect to the SC configuration because of the temperature differences between the crystals as shown by MSX experiment under the direct solar illumination of QCMs. As a matter of fact, with direct Sun illumination of the microbalance field of view, the sensing crystal becomes warmer than the reference crystal and as the temperature difference between the two crystals becomes relevant despite the sandwich layout, the beating frequency changes accordingly. This behavior could to be taken into account in data processing if the crystals temperature were known therefore the need of accurate temperature measurement of the crystal surface, to get rid of the instrumental effect due to the temperature is of outmost relevance. (Scaccabarozzi et al. 2016).

2.3 QCM provider companies

QCM have many applications in industrial, pharmaceutical, biomedical fields and in the study of the terrestrial atmosphere (Vashist S.K. and Vashist P. 2011, Pantalei et al. 2007, Macagnano et al. 2008) Table 4 summarizes the fields of applications and for each of them the achievable measurements goals.

The off-the-shelf QCMs are provided by various industrial companies (e.g. Inficon, Gamry Instrument, NdK, ICM, QCM Research etc.) Tab.5, reports the main manufacturers allowing for a direct comparison of the characteristics and performances of commercially available QCM based sensors.

Table 5 includes the crystal/electrode diameters, thicknesses, materials, frequency resolution, stability and operative temperature range. In addition, suggested applications for each sensor are also given. For instance, INFICON provides Research-Quartz Crystal Microbalance (R-QCM) System, allowing the monitoring of the film properties during the PVD deposition process, dissolutions or permeation, whereas the INITIUM proposes a QCM Affinix Series modules to evaluate the biomolecular interactions and medicine binding. Among the available products and supplier, QCM Research and Crystal Teck Corp. (Faraday Labs.) provide a TQCM (Thermoelectrically-cooled Quartz Crystal Microbalance) and CQCMs (Cryogenic Quartz Crystal Microbalance) systems compatible with space application and missions, where the main limitations arise from the expected working temperature range and mechanical environment (Scaccabarozzi et al., 2014). As demonstrated by Freedman et al. (2008), MK10 (a QCM provided by QCM Research) is able to monitor the vapour pressure and the enthalpy of sublimation of solid substances. Generally, the most important non-space QCM applications include the metal deposition, chemical reaction monitors, electroactive polymers and corrosion studies. In particular, the applications to biomedical field, industries and biomolecular interaction (http://www.initium2000.com/en/AFFINIX_Series.pdf) are focused on the study of protein, DNA, sugar chain, Lipid and enzyme, small molecule, plastic polymers and materials described in Table 4.

Table 4. The different studies applied in the biomedical, industries and biomolecular fields interaction are listed below.

Protein	**DNA**	**Sugar chain**	**Lipid and Enzyme**	**Small molecule**	**Plastic polymer**	**Materials**
Protein interaction	Hybridization	Sugar - Protein interaction	Lipid - Antibacterial Peptide interaction	Evaluation of Inhibi or	Polymer Materials – Biomolecule interaction	Adhesion to Carbon nanotube
Antigen - Antibody reaction	Detection of mismatched base pair	Hydrolysis of Polysaccharides	Liposome binding	Evaluation of Medicine binding	Polymer decomposition	Metal dissociation
Aggregation of β-Amyloid	RNA - DNA and RNA - Protein interactions	Polymerization by Glycosyl transferase	Hydrolysis reaction by DNase	Evaluation of Toxin	Evaluation of Biocompatible Polymer	Evaluation in Crude solution
--	--	--	Elongation reaction by Polymerase	--	Particle's adsorption	Evaluation of effective Detergent

Table 5. QCM suppliers for space and ground applications. Geometrical characteristics of QCMs and crystal diameters, and resonant frequency are listed. The dimensions of QCM modules are also given. The QCMs manufactured by QCM Research Company work in a different operative ranges with respect to the others, thanks to the company space heritage. The crystal configuration are DC and SC and the main QCM suppliers for space applications (red bold color) are QCM Research, CrystalTeck Corp. (Faraday Labs.) and Meisei Electric (JP).

QCM Supplier	**INFICON** (RQCM - Quartz Crystal Microbalance	**CrystalTeck Corporation** (TQCM and CQCM	**QCM Research** (MK10, MK17,	**MEISEI ELECTRIC CO.**	**Owls Sensor (QCM-ITO Crystal)**	**LapTech Precision**	**Gamry Instruments (eQCM)**	**Biolin Scientific Q-SENSE (E1-E4**	**International Crystal Manufacturing Co.**	**INITIUM (QCM Affinix Series)**

	Research System) http://www.inficon.com/en-us/home.aspx	System) http://crystaltekcorp.com/	MK26) http://www.qcmresearch.com/#/home	http://www.meisei.co.jp/english	http://www.owls-sensors.com/	http://www.laptech.com/qcm.php	http://www.gamry.com/	**Module)** http://www.biolinscientific.com/product/q-sense-sensors/	**Inc.** http://www.icmfg.com/quartzmicrobalance.html	http://www.initium2000.com/en/
Configuration	SC	DC	DC	SC	SC	SC	SC	SC	SC	SC
QCM frequency (MHz)	5- 6- 9	15 - 16.8	3-10-15	9	5	from 1 to 30	from 1 to 10	5	5 - 10	27
Crystal Diameter (mm)	25.4 for 5 MHz 14 for 6 MHz 25.4 for 9 MHz	Not available	11.81 (MK17) - 12.70 (MK10)- 11.81 (MK26)	Not available	25.4	from 3.8 to 25.4	25.79 (10 MHz)	14	13.66 - 8.63 - 8.08	--
Mass sensitivity (Hz/ng/cm^2)	0.056 for 5 MHz 0.081 for 6 MHz 0.181 for 9 MHz	0.51 (15 MHz)	0.226 (MK17) 0.226 (MK10) 0.509 (MK26)	0.181	Not available	Not available	Not available	0.05	Not available	Not available
Electrode material	Gold, Platinum, Titanium, Aluminium, Silver (Quartz crystal)	Gold plated (Quartz crystal)	Gold (Quartz crystal)	Gold	Gold (Quartz crystal)	Gold, Silver, Aluminium (Quartz crystal)	Gold (Quartz crystal)	Gold (Quartz crystal)	Gold, Aluminium, Carbon, Chromium, Cobalt, Copper, Silver, Titanium, Zinc (Quartz crystal)	Gold (Quartz crystal)
Electrode Diameter (mm)	12.7 for 5 MHz 6.35 for 6 MHz 12.7 for 9 MHz	Not available	11.81 (MK17) - 12.70 (MK10)- 11.81 (MK26)	Not available	13.4	(1.5×2.5) and (5.0×5.0)	Not available	4.8	3.48 - 5.11 - 6.81	14
Crystal Thickness (µm)	333 for 5 MHz 227 for 6 MHz 185 for 9 MHz	111.3 (15 MHz)	167 (for MK10-MK17 and MK26, 10 MHz)	Not available	334	1670 for 1 MHz 55,7 for 30 MHz	167 for 10 MHz	334	334 for 5 MHz 167 for 10 MHz	61.9
Thickness/Diameter Ratio	0.026 for 5 MHz 0.016 for 6 MHz 0.007 for 9 MHz	--	0.013 (for MK10, 10 MHz) 0.014 (for MK17 and MK26, 10 MHz)	Not available	0.013	0.439 for 1 MHz 0.002 for 30 MHz	0.006	0.024	0.024 - 0.038 - 0.041 for 5MHz 0.012 - 0.019 - 0.021 for 10MHz	--
Dimension Unit (mm)	--	30.5×31.8 (CQCM and TQCM module)	15.75×27 (MK26) 31.75×71.4 (MK10) 21.72×25.27 (MK17)	--	--	50x125	175×115×80 (eQCM Unit)	37×35×63	--	140×300×220 (Affinix QX) 140×300×220 (Affinix QNµ) 360×440×220 (Affinix Q4)
Surface Roughness (A)	Polished (50)	Polished	Polished (MK26)	--	--	Polished		Polished	Polished	--
Operative temperature (°C)	from 0 to 50	from -199°C to +100°C (CQCM) and from -59°C to +100°C (TQCM)	from -60 to +80 (MK26)	from -40 to 65	from 20 to 80	--	from 0 to 45	from 15 to 65	from 0 to 50	0-50 (Affinix QX) 10-50 (Affinix QNµ) 10-40 (Affinix Q4)
Frequency Resolution (Hz)	0.03	0.1	Not available	--	--	--	0.02	0.01	--	--
Mass resolution	0.4 ng/cm^2	--	0.0035 ng/cm^2 CQCM 0.0033 ng/cm^2 TQCM	1 ng (at constant Temperature), 100 ng (over the Total temperature range)	--	--	1	0.5 ng/cm^2	--	30 pg/Hz
Frequency stability	±2 ppm total, over 0º to 50º C	±1	--	--	--	--	--	<1Hz/hr	±2.5 Hz	<1
T resolution (°C)	0.1	0.1	Not available	--	--	--	--	±0.02	--	--
Q factor	120000 for 5 MHz 55000 for 9 MHz	--	--	--	--	--	10^5 (air) - 3×10^3 (liquid)	--	--	--
Coating	--	No	--	No	No	No	Pt, C, Fe, Ti	Aluminium silicate, Au with Ti Adhesion, Barium titanate, Calcium Carbonate	No	SiO$_2$, Ti
Applications	Monitoring the film properties during processes	Non-solid residual contaminants	TQCM and CQCM can easily be		Biosensor system, Surface interaction,	Biomedical Sensors, Metal	Electroactive Polymers,	Evaluation of material properties of	Metal deposition and chemical	Protein-Protein interaction,

	such as deposition, dissolution or permeation	monitors (residues from coatings, adhesives, lubricants and cleaning agents)	adapted for the space flight (Satellite mission, Space Stations and Space Shuttle flight)		electrochemical measurements and optical investigation	Deposition Monitors, Environmental Monitoring and Chemical Reaction Monitors.	Corrosion Studies, Electro deposition, Self-Assembled Monelayers, Antibody-Antigen Interactions, Protein Adsorption, Ion and Solvent Transport	surface coatings and of interactions between a surface and its physiological environment	reaction monitors, biomedical sensors, detection of mass, density, viscosity, adsorption, desorption, and corrosion.	Antigen, Antibody reaction, RNA-DNA and RNA-Proteins reaction, Evaluation of medicine binding, biomolecular interactions, metal dissociation ect.

3. QCMs for space applications

3.1 Historical view, missions and experiments

QCM measurements were performed on many different NASA STS MISSIONS in the period 1981-1997 and on spacecraft close to flimsy instruments in order to measure the contamination levels at various locations and AO or the thruster firings erosion/deposition on sensitive surfaces. The first QCMs launched on NASA's Space Shuttle Program date back to November 1981 aboard the Space Shuttle Columbia and continued with Induced Environment Contamination Monitor (IECM) program that launched different QCMs on flights STS, from 2 to 9. In February 1997 five QCMs (STS-82 flight) were onboard the Space Shuttle Discovery to measure the contamination near the Hubble Space Telescope. Most of the launched QCM were part of larger instrumentation packages. In particular, the QCMs onboard STS-82 allowed measurement of the contaminants in the vicinity of the Hubble Space Telescope during the second servicing mission. Detailed chronological summary of the QCMs sensors launched with NASA Shuttle programs is provided below (missions in bold format are ones for which literature data and experimental results are available and will be discussed in detail) whereas sensors characteristics are summarized in Table 6.

- **STS-2:** **IECM** (Induced Environment Contamination Monitor) - (Miller 1982, Miller 1983)
- STS-3: IECM - CMP (Contamination Monitor Package) - (Kruger et al. 1993, Miller 1982)
- STS-4: IECM (Induced Environment Contamination Monitor) - (Miller 1983)
- **STS-9:** **IECM** (Induced Environment Contamination Monitor) - (Miller 1984, McKeown 1999)
- **STS-32**: **LDEF** (Long Duration Exposure Faclity) – (Levine 1992)
- **STS-46:** **EOIM 3** (Evaluation of Oxygen Interaction with Materials Experiment) - (Green 2001)
- STS-52: SPIE QCMs on the arm - (Green 2001)
- STS-56: Inside SSBUV - (Green 2001)
- STS-62: SSBUV - (Green 2001)
- STS-66: SSBUV - (Green 2001)
- **STS-72:** **REFLEX** (REturn *FLux* EXperiment) - (Benner et al. 1998, Green 2001)
- **STS-82:** **HST** (Hubble Space Telescope) - (Hansen 1994, Green 2001).

Sensors characteristics are summarized in Table 6.

Table 6. Comparison between QCMs used in several Space Shuttle flights. The QCM suppliers and the experimental characteristics (i.e. warm-up rate, regeneration temperature and the coating) are also given. Empty cell means not available data (e.g. Hubble Space Telescope). The DC configuration was used for these missions.

Experiment on STS	**LDEF (STS-32)**	**IECM (STS-2)**	**IECM (STS-9)**	**REFLEX (STS-72)**	**HST (STS-82)**	**OPM (STS-81)**
Configuration	DC	DC	DC	DC	--	DC
QCM frequency (MHz)	10	15	15	15	15	15
QCM Producer	QCM Research	Faraday Lab. Inc.	Faraday Lab. Inc.	Faraday Lab. Inc.	--	Faraday Lab. Inc.
Mass sensitivity (g cm^{-2} Hz^{-1})	4.42×10^{-9}	1.56×10^{-9}	1.56×10^{-9}	1.56×10^{-9}	--	1.56×10^{-9}
Mission Orbit	LEO (470 km)	LEO	LEO	LEO (300 km)	LEO	LEO
Operative temperature (°C)	minimal temperature of each orbit - no specified	-50/+30 (CQCM) +30/0/-30/-60 (TQCM)	-10/-40 (CQCM) and -60 to 80 (TQCM)	+16/+18	+20 CQCM 0 TQCM	-10/-30 TQCM
Resolution f (Hz)	--	±1	±1	±1	--	--
Max mass loading (g cm^{-2})	--	3×10^{-4}	3×10^{-4}	--	--	--
T resolution (°C)	--	±1	±1	±1	--	±1
Warm-up rate	not controlled	0,008 °C/s (cooling and warm up)	0,33 °C/s (cooling) 0,77°C/s (warm up)	--	--	--
Coating	ZnS In_2O_3	gold plated, optically polished quartz crystals	gold plated, optically polished quartz crystals	graphite kapton	--	gold plated, optically polished quartz crystals
ΔF (Hz) and ΔT(°C) for solar pulse	300-500 Hz --	Observed but no received	Observed but no received	500-800 Hz 2°C	-- --	9-100 Hz --
Regeneration T(°C)	--	80	80	--	--	--

Considering the IECM, QCMs used in the experiment were developed by NASA and flown on flights STS 2,3,4,9 and in Plume Impingement Contamination-I (PIC-I, on STS 74), whereas the data obtained from Plume Impingement Contamination-II onboard the LISA Pathfinder, (formerly the mission was called SMART-2, i.e. Small Missions for Advanced Research in Technology-2, finished on 30 June 2017) are still today under elaboration.

The Roscosmos (Russian space agency) launched three different experiments in the framework of the MIR Space Station for contamination monitoring by using QCMs these experiments (Minor 2001, Soares and Mikatarian 1994, Krylov et al. 2015) are grouped with the QCM experiments performed onboard ISS (Table 7) and are listed in the following:

- **PIC** (Plume Impingement Contamination) - (Soares et al. 2003)
- **MEDET** (Materials Exposure and Degradation ExperimenT) (Dinguirard et al. 2001; Inguimbert et al. 2008, Tighe et al. 2009)
- **Astra-II Experiment** (June 1995 – end of 1997)

- **EuroMir 95 Instrument Comrade Active** (ICA) Experiment (September 1996 – March 1996)
- **Optical Properties Monitor (OPM)** (May 1997)

`Table` **7.** Characteristics of QCM used in Space Station Mission (ISS and Mir). Empty cell means not available data. The crystal configuration are DC and SC while the QCM supplier are QCM Research, Faraday Labs. Inc, Applied Geophysics Institute (IPG) and Moscow Aviation Institute (MAI). Data of EuroMir 95 ICA Experiment are not available.

Space Station Mission	**PIC (1995)**	**MEDET (2008)**	**Astra-II (1995)**	**OPM (1997)**
Configuration	DC	SC	SC	DC
QCM frequency (MHz)	10	10-11	--	15
QCM Supplier	QCM Research (MK 16)	Variation of commercially QCM	Applied Geophysics Institute (IPG) and Moscow Aviation Institute (MAI)	TQCM Faraday Labs. Inc.
Mass sensitivity (g Hz^{-1} cm^{2})	4.42×10^{-9}	4.42×10^{-9}	4×10^{-8}	1.6×10^{-9}
Orbit mission	LEO	LEO (400 km)	LEO	LEO
Operative Temperature(°C)	+25	Temp. of RAM direction	0	-30 and -10
Resolution f(Hz)	±2	--	±1	--
Max mass loading (g cm^{-2})	measured	--	4×10^{-8} to $1.6\ 10^{-4}$ g cm^{-2}	--
T resolution (°C)	--	--	--	±2
Warm-up rate (°C min^{-1})	0.02°C/min	--	not thermally controlled	--
Coating	Gold	carbon	--	--
ΔF(Hz) and ΔT(°C) for solar pulse	Correction data for the temperature contribution	--	not directly observed	--
Regeneration T(°C)	>50	present	--	--

After first NASA's Space shuttle flights, numerous QCMs have been applied in satellite missions, in order to test and monitoring new technologies on spacecrafts. Hereafter a detailed list of the available data for the intended application is provided:

- **Deep Space 1 -** (Brinza et al. 2000, Brinza et al. 2001, Buehler et al. 2004)
- Discoverer Satellites (from 1961 to support Atlas Missile program)
- Environment Verification Experiment tor the Explorer Platform (EVEEP)
- Long Duration Exposure Facility (LDEF)
- Spacecraft Charging AT High Altitudes (SCATHA)
- **OGO 6 -** (Mckeown 1998, McKeown et al., 1973)
- **MSX -** (Wood et al. 1997, Wood et al. 1998, Wood et al. 2000)
- **SDS 4 -** (Miura et al. 2013, Nakamura et al. 2013)

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- **SMART 1** - (Gonzalez 2005, Tajmar et al. 2004)
- **LISA Pathfinder** - (Paita et al. 2012, Capacci et al. 2007)

QCM's suppliers, characteristics and performances in seven satellite mission of JAXA (SDS-4), NASA (DeepSpace1, OGO-6, MSX) and collaborations with ESA (SMART 1, LISA Pathfinder and MEDET) are summarized in Table 8. In particular, MSX experiment will be discussed in detail.

Table 8. Characteristics of CQCM and TQCM used in satellite mission. Empty cell means not available data. The crystal configuration are DC and SC while the QCM supplier are QCM Research, Faraday Labs. and Meisei Electric.

Satellite Mission	**SDS-4 (2012)**	**LISA Pathfinder (2015)**	**SMART-1 (2003)**	**MSX (1996)**	**Deep Space1 (1998)**	**OGO-6 (1969)**
Configuration	SC	DC	DC	DC	DC	DC
QCM frequency (MHz)	9	10	10	10 TQCM 15 CQCM	10	10
QCM Supplier	Meisei Electric Co.	QCM Research (MK 17)	QCM Research (MK 17)	QCM Research (MK 16, MK 10)	QCM Research (MK 16)	Faraday Lab. Inc. (Mckeown)
Mass sensitivity (g Hz^{-1} cm^{2})	1 ng (T=const) 100 ng (over T range)	4.4×10^{-9}	4.4×10^{-9}	4.42×10^{-9} TQCM 1.96×10^{-9} CQCM	4.43×10^{-9}	3.5×10^{-9}
Orbit mission	LEO (671 km)	Sun-Earth L1	Moon Orbit	LEO (903 km)	Solar orbit	LEO (polar orbit)
Operative Temperature(°C)	from -40 to+65	from -50 to 120	from -50 to 120	-253 for CQCM -40/-50 for TQCM	from -43°C to +80°C	from -50°C to 100°C
Resolution f(Hz)	--	0.1	0.1	±2	--	±1
Max mass loading (g cm^{-2})	$>10^{-5}$	--	--	3.5×10^{-6} CQCM 3.3×10^{-6} TQCM	$>10^{-4}$	10^{-5}
T resolution (°C)	--	--	--	±0.25	<±0.2	10^{-4}
Warm-up rate (°C min^{-1})	passive	--	--	2.5	--	--
Coating	uncoated	gold	gold	gold	gold	MgFl
ΔF(Hz) and ΔT(°C) for solar pulse	--	--	--	300-450 Temperatures are not available	<250 Temperatures are not available	Decrease of contamination due to solar exposure
Regeneration T(°C)	85	--	--	60	75	100

QCM technology is also gaining interests for the next planned space missions for contamination monitoring (molecular and particulate) and degradation of telescope mirrors, solar panel, detectors and other sensitive surfaces. The next space missions (ESA and NASA contribution) and contamination requirements are listed in Table 9. In particular, the QCM sensors could be used for contamination monitoring of X-ray spectrometer (Solar Orbiter and ATHENA missions), for telescope mirrors (primary, secondary etc.) like in the case of Euclid, JWST and Plato.

Table 9. The next space mission including the objectives and the contamination requirements are listed (Holmes et al. 2016, Wooldridge and Aremberg 2008, Sørensen 2010, Peyrou-Lauga and Darel 2017, ATHENA: Mission Budgets Document, ESA-ESTEC 2017, https://www.jpl.nasa.gov/missions/euclid/,

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https://www.nasa.gov/feature/goddard/nasa-technology-protects-webb-telescope-from-contamination, https://www.jpl.nasa.gov/missions/wide-field-infrared-survey-telescope-wfirst/).

Space mission	**Launch**	**Type**	**Objective and Research field**	**Sensitive surface**	**Contamination limit**
Euclid (NASA-ESA)	2020	orbiter	dark matter and dark energy	1.2 m (dimeter) telescope and infrared flight detectors	<5 μg cm^{-2} (molecular) 5-50 μg cm^{-2} (particulate)
Solar Orbiter (ESA)	2020	orbiter	high-resolution studies of Sun and inner heliosphere	Energetic Particle Detector (EPD), X-ray spectrometer/telescope (STIX)	300 ng cm^{-2} year^{-1}
JWST (NASA, ESA, Canadian space agency)	2020	spacecraft	universe at near and mid-infrared wavelengths (L2)	Korsch Telescope (mirrors)	200 Angstroms per each mirror
WFIRST (NASA)	2020	orbiter	dark energy, exoplanets, and infrared astrophysics	telescope (primary mirror of 2.4 meters), Wide Field Instrument, and the Coronagraph Instrument.	to be determined
JUICE (ESA,NASA)	2022	orbital spacecraft	Jupiter system	sub-millimiter wave instrument (SWI) and Moons and Jupiter Imaging Spectrometer (MAJIS)	to be determined (contamination and decontamination heaters)
Plato (ESA)	2024	spacecraft	extrasolar planetary systems	Main telescope (multiple refractors)	500 ppm (particulate) 1 μg cm^{-2} (molecular)
ATHENA (ESA, NASA)	2028	spacecraft	hot gas structures supermassive black holes (L2)	X-ray Spectrometer	50 ppm (particulate) 4 μg cm^{-2} (molecular)

3.2 QCMs on Space Shuttle flights

3.2.1 LDEF (STS-32)

The Long Duration Exposure Facility (LDEF) was a school bus size cylindrical facility that flew on STS-32 and represented an opportunity to examine type and amount of contaminants accumulated during 6 years in orbit. It was placed in LEO by Space Shuttle Challenger in April 1984 and retrieved by the Space Shuttle Columbia in 1990. LDEF's 69 months orbit duration provided scientific data on the long-term effect of space environment on materials, components and systems that has benefited NASA spacecraft designers to these days (Stuckey et al. 1993a).

The QCM sensor heads selected for the mission (LDEF M0003-14 manufactured by QCM Research) exploited two types of coating: 1. one set of crystals for the leading and trailing edge of the spacecraft consisted of crystals with 9,000 Å of aluminium and aluminium oxide ($Al + Al_2O_3$) and a top layer of 150 Å of indium oxide (In_2O_3); 2. the second set of crystals on the leading and trailing edges consisted of 9,000 Å of $Al + Al_2O_3$ and a top layer of 150 Å of zinc sulfide (ZnS) (Fig.4) (Stuckey et al. 1993b). The crystals with the In_2O_3 coating

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were selected for the on-orbit data acquisition. The QCM sensor head consisted of a pair of crystals, one exposed to the environment, i.e. the "sensing" crystal, and the other one unexposed, i.e. the "reference" crystal. The beat frequency between the used crystals was monitored and represented the change in mass as a result of exposure in space environment. The first QCM sensor head response was recorded during the first 424 days of the mission while the second QCM sensor head (ZnS coated) was also flown but not monitored. After the flight, the QCMs sensor heads were disassembled and analysed in the Aerospace Corporation Laboratories.

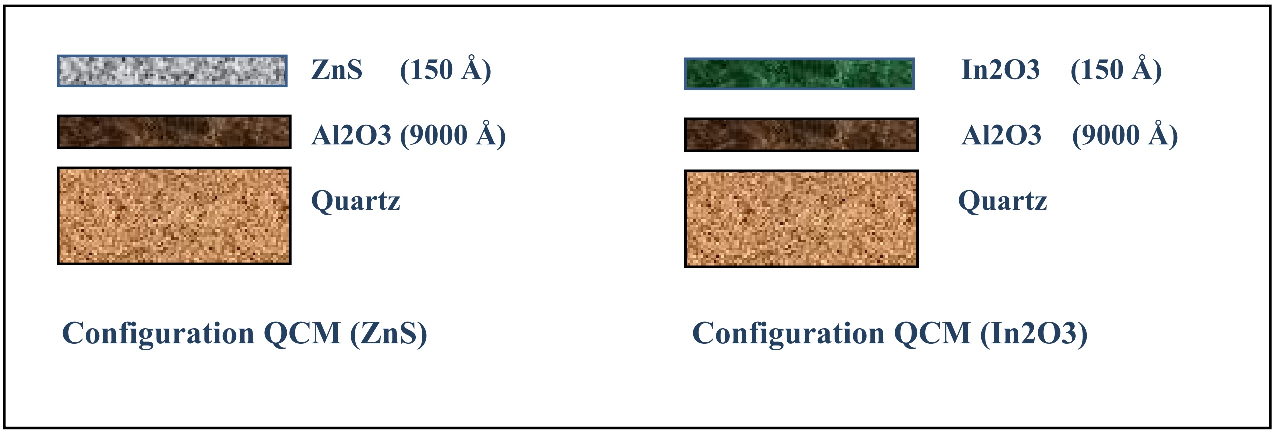

Figure 4. **(from Levine 1992)**. The configuration of two QCMs used LDEF have been reproduced with the coated materials, eroded by the atomic oxygen in the upper atmosphere [This figure is taken from NASA-CP-3134-PT-3, “LDEF: 69 Months in Space. First Post-Retrieval Symposium”, A.S. Levine and used with permission of NASA].

The QCM temperature was not controlled (was allowed to "float" with the spacecraft) causing a subsequent change in QCM output frequency on the order of 300 to 500 Hz (Green 2001). The frequency data acquired during the mission are shown in Fig.5, corresponding to the maxima (dashed line) and minima (continuous line) temperature recorded for the leading and trailing edge during each orbit (Stuckey 1993). The trailing edge QCM indicated a slight increase in weight during the 424-day data acquisition period while the leading edge showed an apparent weight loss (~ 1 Hz per day). Both the In2O3 and ZnS surfaces have been analysed with similar results with respect to contamination (Hemminger 1992). In particular, silicon was detected on both the leading-edge and trailing-edge surfaces, with higher concentration of silicon on the leading edge surface.

Moreover, the results showed that the cleanest area at LDEF had less 100 Å of contaminants deposition while other areas were heavily contaminated. Large pieces of debris were generated by AO erosion on LDEF surfaces (during in-orbit activity) and the molecular deposits was found around tray vents from the LDEF interior or from the trays themselves. The flown QCMs showed that the accumulation was still measurable after one year in orbit: testing at the leading edge provided higher contamination levels in some cases apparently due to the back flux of contaminants (Stuckey et al. 1993).

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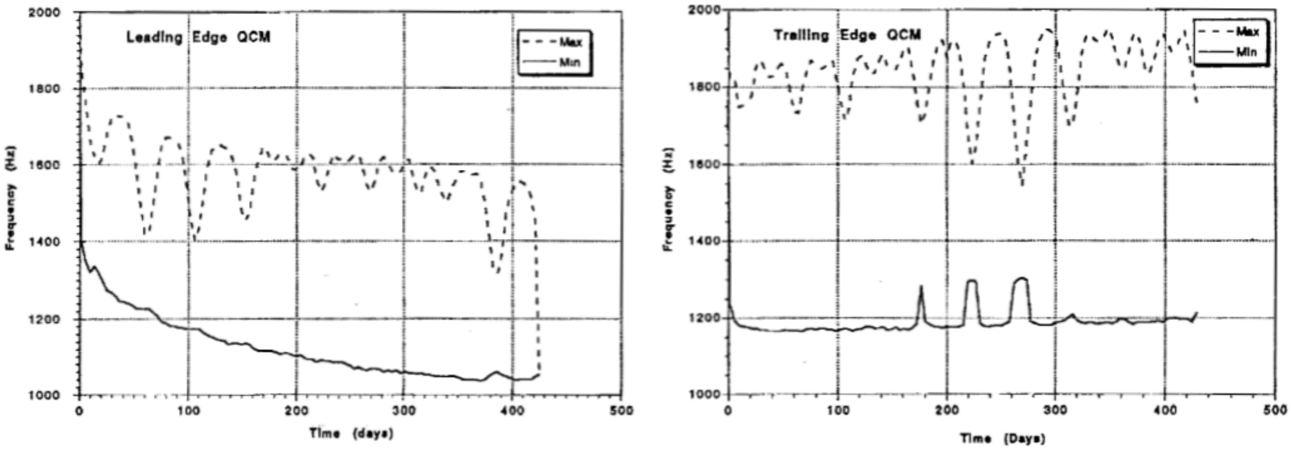

Figure 5. (from Stuckey 1993b). *Left*: Leading-edge quartz-crystal microbalance frequency change. *Right*: Trailing-edge quartz-crystal microbalance frequency change. Acquired data, corresponding to minimal temperature (excluding the solar exposure) show in trailing edge increase of the QCM frequency (due to mass deposition) for the entire period whereas, in the leading edge, continuous material loss was found [This figure is taken from NASA N93-29684, "Post-flight analyses of the crystals from the M0003-14 quartz crystal microbalance experiment", Stuckey, W. K.; Radhakrishnan, G.; Wallace, D. and used with permission of NASA].

3.2.2 EOIM-3 (STS-46)

The Evaluation of Oxygen Interaction with Materials Experiment (EIOM-3, the third of EOIM missions) flew on STS-46 (launched on 31st July 1992) to investigate the materials degradation phenomenon. The Environment Monitoring Package (EMP), was flown on as a part of instrumentation to measure the materials interaction and degradation due to AO. The EPM was equipped with 5 TQCMs with resonance at 10 MHz, which were used to monitor the erosion rates of materials coated on their sensing crystals. The applied coatings were Polyurethane, Kapton, Carbon, and Teflon (Green 2001). The 5th TQCM was left uncoated and was used as reference. The STS-46 mission provided a total exposure time of 42.3 h and the estimated AO 2.2 - 2.5×10^{20} atoms cm^{-2} based on atmospheric modelling, was revealed by on-board mass spectrometer and caused Kapton materials film erosion. The EOIM-3 was returned to earth for post flight analysis (Barna and Pauleau 1996).

3.2.3 REFLEX (STS-72)

STS-72 was launched on 11st January 1996, and hosted the OAST Flyer payload that comprises four experiments, i.e. the Return Flux Experiment (REFLEX), the GPS Attitude Determination and Control System (GADACS), the Spartan Packet Radio Experiment (SPRE), and the Solar Exposure of Laser Ordinance

Devices Experiment (SELODE). The REFLEX experiment was able to detect the contamination process and erosion of coatings as a result of reaction with AO and the molecules from the "return flux" process.
REFLEX experiment included several instruments, one of which consisting in three TQCMs (with a resonant frequency of 15 MHz and manufactured by Faraday Labs.) equipped with built-in platinum resistance temperature sensors: the first TQCM (named A with reference to Fig.6) was coated with graphite and placed on the left side of the package, the second TQCM (named C) was coated with Kapton and placed on the top nearest the middle of the package and the remaining TQCM (named B) was uncoated (to be used as reference). The latter sensor was placed on the top as well, near the TQCM C.

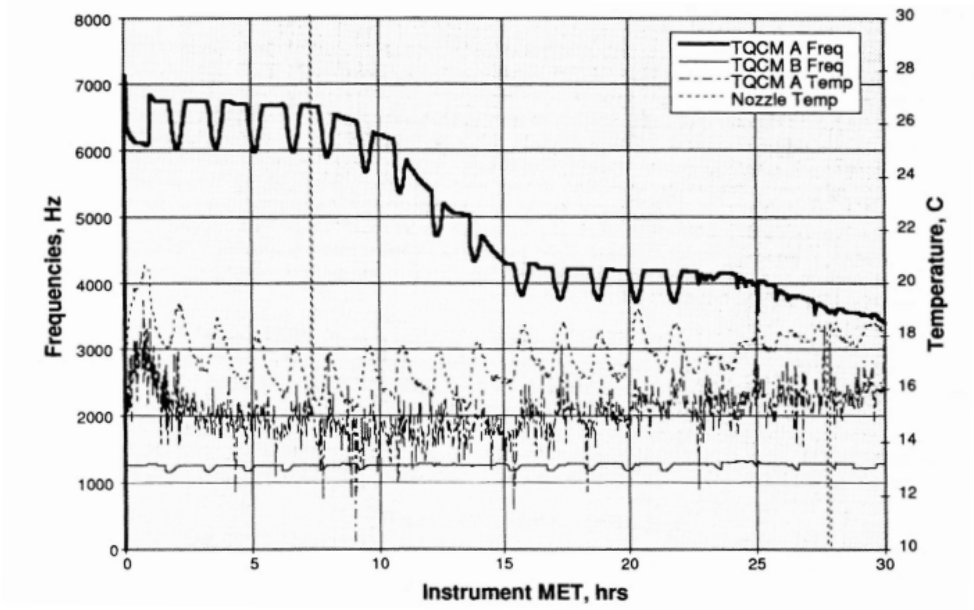

Figure 6 (from Benner at al. 1998). The REFLEX experiment where three TQCMs were placed in different locations in order to monitor the return flux of contaminants. *Right*: Measured temperatures and frequencies for TQCM A and B. Due to the solar exposure, the TQCM A temperature varied of about 2°C, leading to a frequency variation between 500 and 800 Hz and causing misleading data interpretation.

For this experiment, the UV effects were assumed to be negligible since the TQCM was exposed to the sun for very short periods of time, and UV fixing was not readily available on the TQCM. During the 15 hours of exposure, TQCM A frequency decreased from 6800 to 4000 Hz (Fig.6) whereas the TQCM B showed almost no variation during the same time period. This allowed assuming that the effect of contaminant accumulation on the graphite-coated TQCM was negligible. TQCM C showed a small erosion, i.e. about 10% of the erosion shown by the graphite-coated TQCM. Because of the AO exposure times were too short, it was difficult to obtain significant erosion rates for the Kapton. Due to the solar exposure, the thermistor located near TQCMs A and B (in proximity of the nozzle), showed a periodic increase of about 2°C (Benner et al. 1998). These temperature variations corresponded to the periodic decreases in the TQCM frequencies, indicating that the true cause of this variation was actually related to the Sun exposure. In the first part of the analysis, the erosion rates were measured for four different ram angles (18°, 20°, 61°, and -62°) and found to be both consistent and repeatable, i.e. the average graphite volume loss for the 61° and -62° ram angles is 2×10^{-8} cm^3 h^{-1} while for the

18° and 20° angles is 8.5×10^{-8} cm^3 h^{-1} (consistent with previous flight data on carbon, e.g. LDEF) (Manning et al. 2002). The second part of the analysis was devoted to correlate the erosion rate of the graphite with the instantaneous AO density and ram angle. Thus, carbon volume loss as a function of both atomic oxygen density and ram angle was derived. Moreover, the carbon volume loss was analysed as function of AO flux and ram angles and plotted in a 3D graph (see Figure 7): a maximum of volume loss, i.e. 1.6×10^{-7} cm^3 h^{-1} was calculated for a ram angle of 0 degrees and an AO fluence of 3.52×10^{17} atoms h^{-1} (Manning et al. 2002). The obtained result was of primary importance to provide an AO sensor able to measure the AO fluence directly on-orbit.

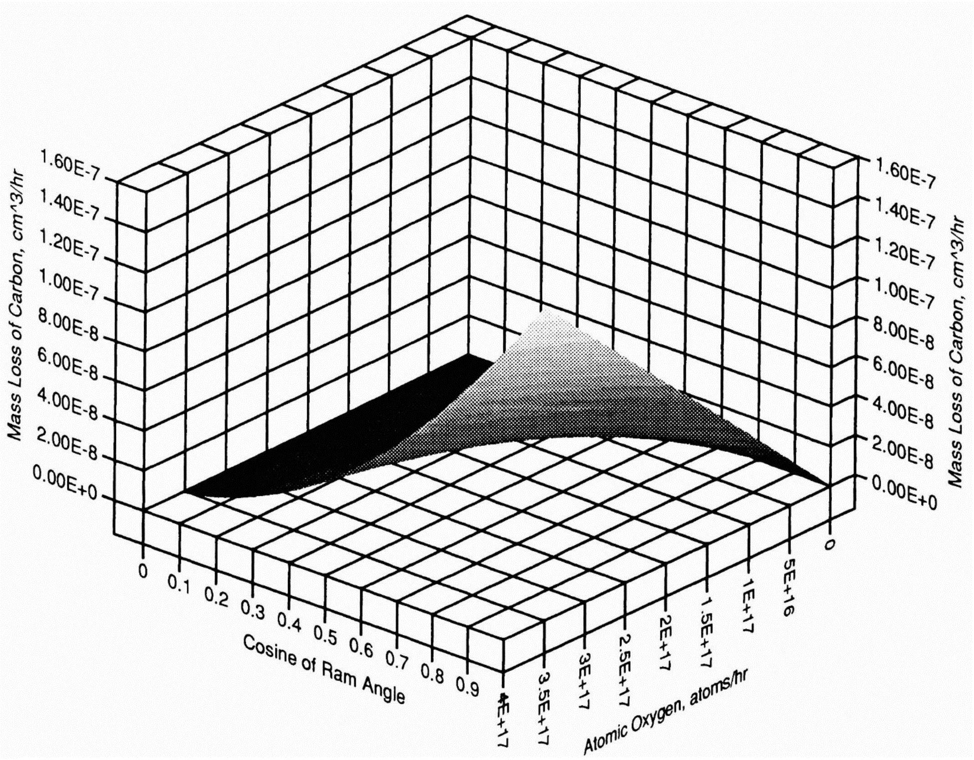

Figure 7 (from Benner et al. 1998). The 3-D plot of carbon volume loss as a function of both atomic oxygen density and ram angle

3.2.4 IECM (STS-2,9)

The Induced Environment Contamination Monitor (IECM) was developed by NASA and flown on Space Shuttle flights STS 2, 3, 4, and 9, to monitor contamination during the space flights. This experiment included 5 TQCMs and 2 CQCMs (Cryogenic Quartz Crystal Microbalance) and was mounted in a payload having dimensions 121×82×79 cm. Results for flights STS 2 and 9 (SpaceLab 1) are hereafter discussed.

In the **STS-2** mission, each QCM sensor head consisted in two matched crystals: a sensing crystal, exposed to outer space, and a reference crystal, placed inside the package (DC configuration, 15 MHz provided by the Faraday Lab. Inc.). Five TQCMs were included in IECM to measure the molecular absorption in each axis of the Orbiter: +X, -X, +Y, -Y, -Z. The sensor mounted in -Z axis operated intermittently and although some data

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were obtained, they were not included in the reference report (Miller, 1982). The temperature of each sensor was controlled by a thermoelectric device so that contamination was measured as a function of temperature: four temperatures were identified, i.e. +30°C, 0°C, -30°C, and -60°C. TQCMs sensors were able to perform five cycles in a total time of 11.5 h. The crystals surfaces were cleaned up at 80°C, afterwards a collection (2h 30m duration time) was programmed (Miller 1982).

The output frequency of TQCMs were affected by many factors, such as the sensor orientation, direction, and distance from contamination sources. Moreover, the radiation intensity from Sun or reflected from Earth affected measured crystals resonance.

In fact, the frequency variation due to temperature changes made the retrieval of the absorbed mass tricky. This occurred especially when the Space Shuttle came out of the Earth's shadow and crosses the night/day terminator. Therefore, the total adsorbed mass was determined at each temperature. The frequency variations obtained at each temperature from the four sensors were averaged together. Figure 8 shows the different behaviors of output of the four TQCMs, being the mass absorption decrease more significant at +30°C and 0°C (the Shuttle-Sun effect is less significant to -60°C and -30°C). Due to lower working temperatures and thermal cycles performed, the deposited mass resulted much higher for TQCM maintained at -30 and -60°C, i.e. ~100 ng cm^{-2} (instead of ~60 ng cm^{-2}, measured on TQCM at 0 and +30°C).

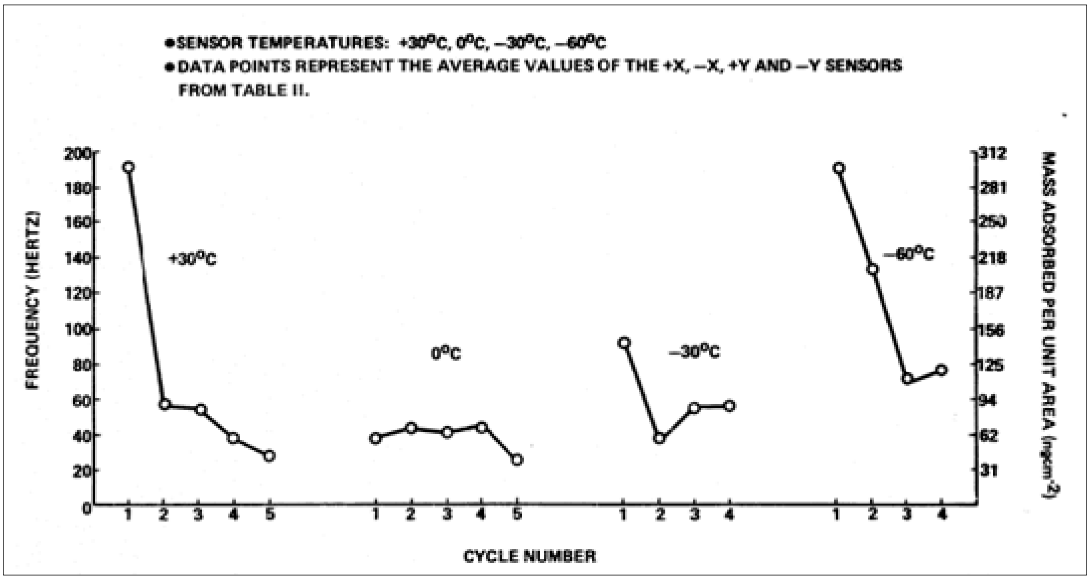

Figure 8 (from Miller 1982). Summary of the average values of TQCMs frequency measured in STS-2. The Sun exposition affected less the TQCMs held at 0°C and +30°C, whereas a stronger frequency variation (due to the temperature increase) was observed for the TQCMs at -30°C and -60°C. [This figure is taken from NASA TM-82457, “STS-2 Induced Environment Contamination Monitor (IECM): Quick-Look Report”, Miller E.R. and used with permission of NASA].

QCM sensors were used also in **STS-9** to monitor the contamination from the empty Cargo Bay in order to verify that the contamination level was within the acceptable limit for the scientific payload. The output signal

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was the beating frequency between two crystals and the main goal of the five TQCMs and two CQCMs was to monitor volatiles contamination levels, respectively. They both consisted in 15 MHz crystal, having a sensitivity of 1.56×10^{-9} g Hz^{-1} cm^{-2}, a maximum allowed load of 3×10^{-4} g cm^{-2} and a frequency resolution of 1 Hz. The TQCMs were temperature-controlled and operated at a predetermined temperature steps between -60°C and +80°C, in order to detect low-volatile contaminants, such as lubricants and epoxies, and were pointed toward the Orbiter axes +Y (right), -Y (left), +X (fore), -X (aft) and -Z (vertical). Moreover, two CQCMs were used to detect the water vapor and CO_2 and were not temperature-controlled. They used a passive radiator to cool its sensors below -100°C when pointed into deep space (Miller 1984).

The amount of contamination measured on STS-9 was significantly larger than other STS mission where IECM flew: about 28000 ng cm^{-2} (over 1700 percent greater than previous flight, +X direction). From the 170 h 25 min to the 177 h of the Mission Elapsed Time (MET), the Hot Test were conducted on the sensors turning the -Z axis into the Sun. In this flight the Orbiter was almost in full Sun and viewed the Earth for just a few minutes per orbit: in this condition the surface temperatures were larger than 80°C and the material outgassed from various components of the spacecraft (IECM was turned off because the maximum temperature was reached). After the contamination deposition, the 71% of the adsorbed contaminants remained on the sensors even after four hours of Sun exposition: the UV radiation performed a polymerization, fixing the contamination to the surface. In this period, the TQCM in +X, -Y and Y direction, collected the most contamination whereas, the for -X and -Z axis sensors showed negligible collection.

The analysis on ground, performed with Scanning Electronic Microscope (SEM) for TQCM in +X direction showed composition of collected particles: Silicon, Aluminum, Magnesium, Zinc, Sulfur, Titanium and Chlorine (e.g. the Aluminum particles had a diameter ranging between 0.5 µm and 2 µm and hundreds of µm in size for Zinc particle).

The CQCMs were monitored from +37°C to -83°C: the maximum temperature was +37°C in the first hours and during the Hot Test while the minimum temperature value was reached during the cold test from 35 h 21m to 58 h 46m MET (-Z1 sensor). Generally, the CQCMs temperature was between 10°C and 40°C: in this case the contamination deposition (on the -Z axis) is less than 4 ng cm^{-2} h. This result was in good agreement with the relatively little contamination arriving from the -Z direction of the TQCM sensor.

Thus, it can be said that the molecular contamination was significant when solar heating was present directly on the bay or by angle of 45° from the -Z axis, where the contamination by redirection was small. At the maximum operating temperature (i.e. 80°C) in 244 h of total flight, the TQCMs collected a total mass of 39 ng cm^{-2} (Mckeown 1998). Most of the particles were condensed volatiles even if, a few refractory grains were collected and analyzed, too. In the total time of flight (244 hours) 39 ng cm^{-2} and 16.4 ng cm^{-2} of contaminants were measured on the +X and -Y axes, whereas, the -X and Z directions showed the lowest collected mass, 1.6 ng cm^{-2} and 1.2 ng cm^{-2}

The probable source of the contaminant particles was the solid rocket firings. From the laboratory analysis of this molecular compound it was possible to detect a strong CH_2, CH_3 and carbonyl absorption bands indicating

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presence of ester and polyester compounds, typically found in adhesives and plasticizers. Most of these particulate had a size between 1 μm and 20 μm and was composed mainly of Mg, Al and Si.

3.2.5 Hubble Space Telescope (STS-82)

A set of 15 MHz QCMs were used to monitor the contamination on Hubble Space Telescope (HST) primary mirror (PM) and secondary (SM) mirrors. The Servicing Mission 2 on the HST was performed in February 1997 during the STS-82 Space Shuttle mission, where the Contamination Environment Package (CEP) was mounted close to the HST, in order to monitor the contamination environment. The CEP included five QCMs and a pressure gauge. Two of the QCMs were maintained at a temperature of -20°C whereas the other 3 were maintained at 0°C (Green 2001). The QCM at -20°C, located on the external surface measured an outgassing rate lower than 1 Hz h^{-1} whereas, the other QCMs frequency (2-3-4) showed constant behavior.

3.3 QCMs on Space Stations (ISS and Mir)

3.3.1 PIC experiment

A fundamental operation in space missions is the quantification of contaminant material deposited on the spacecraft external surfaces from “non-quiescent” sources. In particular, an accurate prediction of thruster induced contamination is required. According to the International Space Station (ISS) external contamination control requirements, the molecular deposition on sensitive surfaces from all contaminant sources is limited to 130 Å per year (Soares and Mikatarian 2003). During “quiescent” period (periods of nominal Space Station operations, which includes material outgassing and nominal venting) the molecular deposition rate is limited to 10^{-14} gr/cm^2/s that translates to approximately 30 Å per year (Soares and Mikatarian 2003). During the “non-quiescent” period (where significant disturbances are introduced to the environment, i.e. Space Shuttle and visiting vehicle proximity operations, ISS re-boost and attitude control), the molecular deposition rate is limited to 10^{-6} gr/cm^2/year (that translates to 100 Å per year). In this scenario, the PIC (Plume Impingement Contamination) flight experiment was conducted during the STS-74 mission in 1996 and aimed to measure the plume induced contamination from the Mir Station (130-N Russian) and Space Shuttle Orbiter PRCS thruster firings by using two pairs of matched QCMs (Soares et al. 2003) to evaluate induced contamination risks for ISS.

In the first experiment of PIC, 100 pulses (each during 0.1 s) from the Russian 130 N thruster were sent to the QCM distant 12.2 m in 10 cycles of 10 pulses, with a one-minute period of interval between the cycles. The cycles caused frequency peaks, whereas a rapid evaporation of exhausted contaminants occurred during the one-minute interval. Summing the measured frequency variations for the 10 cycles (not including the evaporation period) 580 Hz was obtained, corresponding to a deposition of 2.56 μg cm^{-2}. During the cycles,

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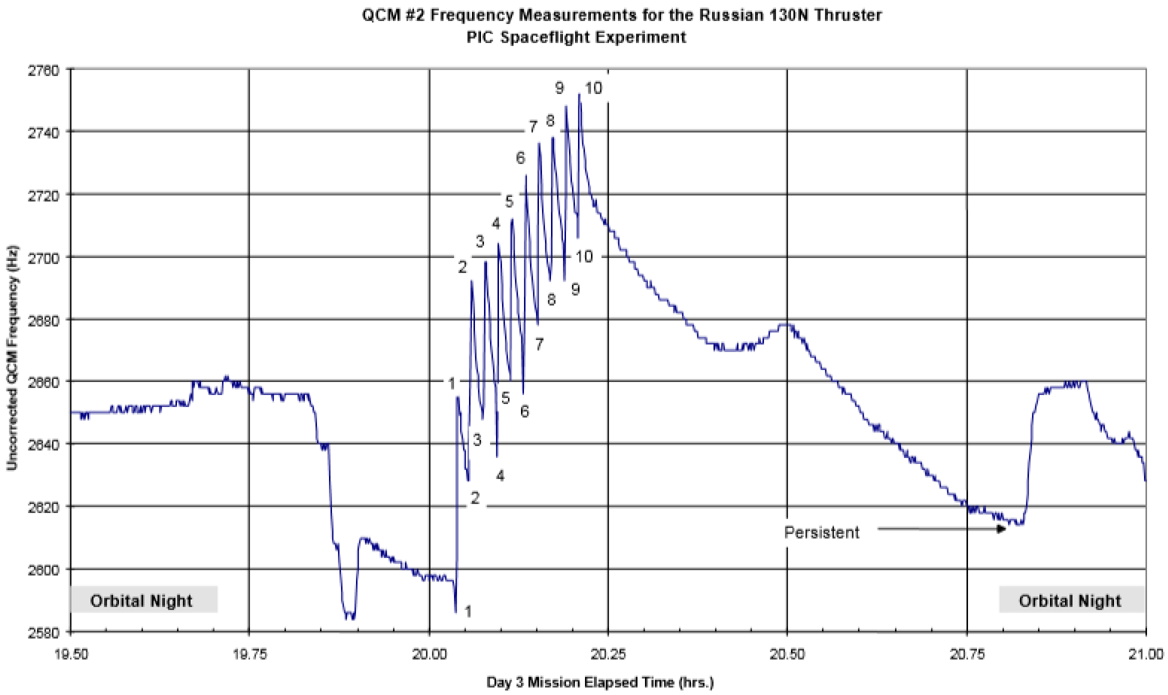
with the QCM at 20°C, 79.3% of the mass deposited was evaporated while, other mass evaporated after performing QCM regeneration at 52°C (see Fig. 9).



`Figure 9` (from Soares et al. 2003). The figure shows the ten pulses (100 ms duration) that correspond to ten cycles of the thrusters' firings. Decrease in frequency during the evaporation period is not included in this computation because it is related only to the evaporation of the deposited contaminant. The final trend shows presence of persistent materials (refractory) after the regeneration.

After the regeneration cycle and the thruster firings, the frequency difference (28 Hz) was corrected for the temperature effect and produced a total variation of 48 Hz, indicating the presence of 0.193 µg cm^{-2} of more refractory contaminants (i.e. 7.5%). This evidenced that the regeneration cycle up to 325 K was not sufficient to allow the evaporation of all the contaminants.

PIC also measured the contaminants deposition by the thruster firings of the Orbiter PRCS. In this case, the QCM was positioned at 10.58 m from the nozzle exhaust plane, and firing of two groups of ten 80 ms pulses was performed for a total thruster time of 1.6 s. Excluding the observed evaporation during the interval between firing groups (45 s), frequency increase of 3802 Hz was measured, corresponding to a total mass deposition of 20.515 µg cm^{-2}, i.e. a contamination flux of 12.82 µg cm^{-2} s^{-1} (at 10.58 m). The temperature correction was not performed because the QCM temperature showed small variation, i.e. about 7°C only. The residual frequency variation after the regeneration was 72 Hz, providing final mass deposition of 0.384 µg cm^{-2}for 1.6 seconds of total time. Finally, the ratio between the permanent material and the initial deposit was only about 1.9% (refractory component), a value lower than the result of the Russian 130-N thruster.

In order to characterize the damage caused by the thruster firings particles, additional testing was performed. In fact, features from droplet impacts during the PIC flight experiment were observed on the camera lens of Orbiter Remote Manipulator System (RMS). Thus, Kapton and Aluminum coupons were placed above the

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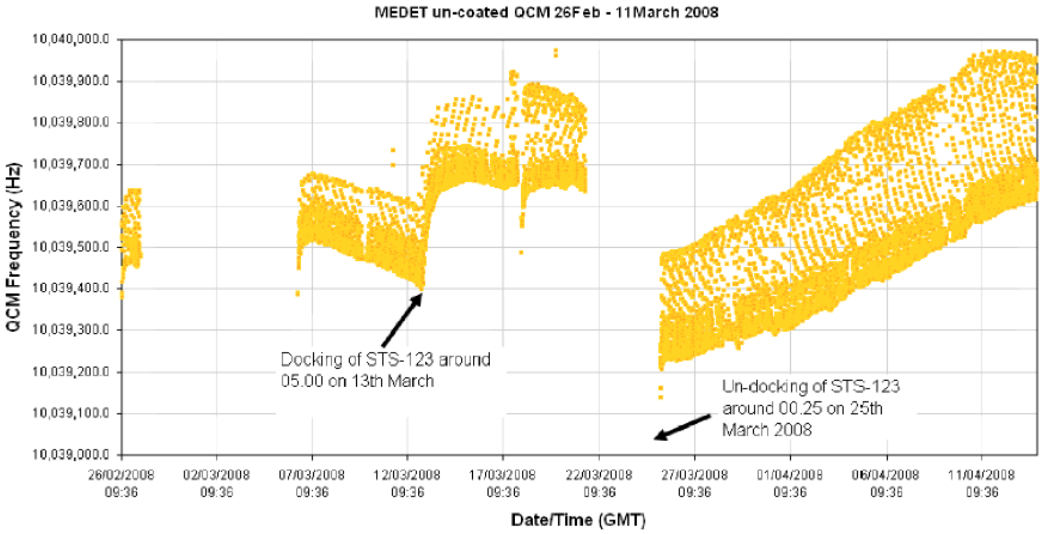
plume direction in order to expose it at the firings (101 in total) with the aim to characterize the induced contamination and droplet impact features. The damage was produced by high-speed droplet impacts and in the case of the Kapton samples, were also produced by chemical reaction between the substrate and the propellant. The analysis with Scanning Electron Microscope (SEM) showed small (<4 µm), medium (5-10 µm) and large craters (11-20 µm).

3.3.2 MEDET experiment

Contamination was monitored by one group of three different QCMs in the MEDET experiment performed on the ISS (2008-2009). The three QCMs were exposed in the RAM direction (i.e. the travel direction of the ISS) and acquired data every 4 minutes. The QCMs group consisted of a gold-coated 10 MHz crystal (sensitivity of 4.42×10^{-9}) to monitor the thruster firings contamination in the vicinity of MEDET module (Type 1), a carbon-coated 10 MHz crystal (Type 2) to measure atomic oxygen (the sensitivity was 2.46×10^{15} O-atoms cm^{-2} Hz^{-1}), and a 11 MHz crystal gold coated (Type 3) used as temperature reference (sensitivity of 600 Hz/K) for raw data (from Types 1 and 2) correction (Dinguirard et al. 2001, Inguimbert et al. 2008). All the crystals were equipped with a heater and thermostat placed underneath the crystal in order to regenerate the sensors by evaporating off the excess deposits of contaminants.

The obtained results (Fig.10) indicated that during a period of several weeks there was a linear relationship between the frequency variation due to the contaminants and due to the temperature effect. Frequency of the temperature contribution (data of QCM3) against frequency of the contamination (data of QCM1) for different orbital cycle of the mission is shown in Fig. 10 as well.



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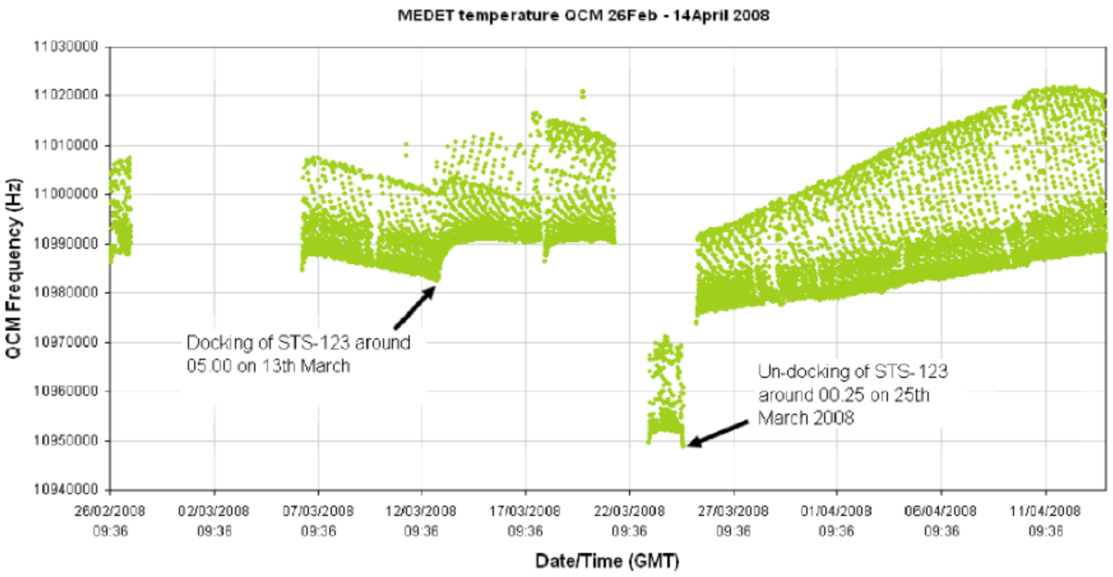

Figure 10 (from Tighe et al. 2009). Frequency of Type 1 (top) and Type 3 (bottom) QCMs in the MEDET experiment as function of time. The temporal behaviors of the measured frequencies of sensing and reference QCMs are similar, suggesting that the differences between the microbalances are almost exclusively due to thermal variations.

After several cycles, a linear relationship was observed with a vertical shift for the longer period, the latter explained with the increase of the contaminant frequency; anyway it was not clear if the obtained result was correlated with the dynamic absorption/desorption phenomena (Tighe et al. 2009). On the contrary, in the first two weeks of exposure, the carbon coated microbalance showed an increase of the frequency, indicating a linear decrease in the mass of carbon due to the erosion caused by atomic oxygen. A gap was present between the Space Shuttle docking and un-docking, but no explanation had been found for that. Finally, analyzing Type 1 and Type 3 measured outputs, it can be noted that the trends are similar and linked together by the environmental temperature fluctuations of the Space Shuttle docking and un-docking. This result testifies the high sensitivity to temperature variation of the QCMs.

3.3.3 Mir Space Station contamination observations

A series of external contamination measurements were performed on Mir Space Station and has been shown to exceed ISS external contamination control requirements by orders of magnitude (Soares and Mikatarian 2000). Mir contamination observations include results from a series of experiments by using QCMs: EuroMir '95 Instrument Comrade Active (ICA), the Russian Astra-II and Optical Properties Monitor (OPC) experiment. Results of the measured deposition rates are summarized in Table 10. Comparing the results of in-orbit testing with the Mir contamination database, the Team was able to identify the contamination sources. Once Mir

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contamination sources were identified and characterized, activities to assess the implications for ISS were implemented.

Table 10. Mir contamination Observations (Soares and Mikatarian 2003).

QCM - Mir contamination experiments	Permanent Deposition (Å)	Deposition rates (g cm^{-2} s^{-1})	On-orbit exposure (months)
QCM 1 (EuroMir '95 ICA)	13	7.8×10^{-11} to 1.2×10^{-10}	3
QCM 2 (EuroMir '95 ICA)	14,5	8.5×10^{-11} to 1.3×10^{-10}	3
QCM 3 (EuroMir '95 ICA)	4,5	3×10^{-11} to 1.8×10^{-11}	3
QCM2 (Astra-II)	5	7×10^{-13} to 8.3×10^{-12}	13
TQCM 1 (OPM)	~80	not available	8.5
TQCM 2 (OPM)	~80	not available	8.5

The Euro-Mir '95 started in September 1995 and was completed in March 1996. ICA QCMs were included in the European Science Exposure Facility (ESEF) platform and located on the end-cone of Mir Spektr module. The QCMs in-flight data were available from October 1995 to January 1996: the QCM1 and QCM2 were directed along the Spektr module axis (ram) while QCM3 was directed perpendicular to the Spektr axis (nadir direction). The increase of QCM frequencies, well correlated with temperature increase due to Mir “solar cycles” (periods with no time in shadow lasting several days), and the pressure readings by Spektr module indicated a significant material outgassing from within the non-pressurized endcone (Soares and Mikatarian 2000).

The Astra-II QCMs had been operating since June 1995 and located on the endcone of Spektr module, on the opposite side from the ICA flight experiment. The QCM2 was directed along the Spektr module axis whereas the QCM1 was directed perpendicular to the Spektr axis (Zenith direction) (Soares and Mikatarian 1994) and performed deposition measurements for about two years. Although the QCMs were not thermally controlled and sensor operating temperatures were not measured the Astra-II pressurized unit was maintained at temperatures above 0°C (Dushin et al. 2006). Because of the abnormal QCM1 behaviour (out-of-range readings) from August 15, 1995 during a solar orbit (solar orbit means that shadow duration on orbit is zero or near zero, as opposed to the usual half-hour), the QCM1 data were considered unreliable. On the other hand, QCM2 showed slow mass increase. In particular, Astra-II measurements showed periods with significant increases in contaminant deposition rate with the presence of solar illumination. Thus, the data collected in these periods have been analysed and correlated with solar orbits (the QCM probably was in local shadow simultaneously with the surfaces in its field of view being heated by the Sun). Conversely, during a period from March through June of 1997, a loss of accumulated mass on QCM2 was recorded when surfaces within its field-of-view were in solar shadow most of the time (Dushin et al. 2006). Only the relevant acquisition of QCM2 are reported in Table 9.

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The Optical Properties Monitor (OPM) was flown on the Russian Mir Space Station to study the long term effects of the natural and induced space environment on materials and also to monitor selected components of the environment including the molecular contamination (Green 2001). The OPM was transported to Mir in January 1997 on STS-81 and exposed on the exterior of the Mir for 8.5 months and returned to ground on STS-89 later that month.

The molecular contamination was controlled by using two TQCMs (15 MHz) manufactured by Faraday Laboratories and maintained at -30°C and -10°C (±2°C) with 1.6×10^{-9} g cm^{-2} Hz^{-1} sensitivity. The condensed mass on the QCM was followed by a re-evaporation due to volatile species that were not fixed on the surface by solar UV.

Two main deposition occurred, i.e. on June and December 1997. The deposition of June 1997 occurred when the Mir was in sunlight for the complete orbit, i.e. the Mir surfaces became significantly hot, increasing outgassing rates. As a consequence, a film thickness growth of 145 Å was obtained on the -30°C sensor (Wilkes and Zwiner 2001). The deposition occurring on December 1997 was by far the largest TQCM event recorded in the OPM experiment. The deposition occurred instantaneously (but rose over 28 minutes to its peak) and represented two mass gain events of 380 Å and 250 Å for the -30°C and -10°C TQCMs, respectively. Then, the deposited film re-evaporated almost completely. Attempts to correlate the measured mass gain events with Mir mission events had been ineffective, mainly because of synchronization problems between the OPM clock and Mir mission.

Except the major mass gain events, a fairly uniform accumulation rate for both the TQCMs was obtained, resulting in contaminant thickness increase of about 20 Å per month (Wilkes and Zwiner 2001). This contamination level was lower than might had been expected from other measurements on Mir mainly because of the view factor of TQCMs on old Mir module well baked-out (6-11 years), and minimum solar UV for most of the mission exposure on the OPM and TQCM, which resulted in a low-fix of contaminants onto TQCM surface (to prevent re-evaporation).

3.4 Satellite applications

3.4.1 OGO-6

The first application of QCMs for space contamination measurements concerns the Orbiting Geophysical Observatory (OGO- 6), launched by United States in 1969, where QCMs to support the Gas-Surface Experiment measuring satellite drag (Mckeown 1998).

Four QCMs (10 MHz, mass sensitivity of 3.5×10^{-9} g cm^{-2} Hz^{-1}) produced by Faraday Lab. Inc. (CrystalTeck Corp.) were used to monitor solar panels contamination, correlating the phenomenon with the eclipse period of the satellite.

The operating temperature tested in laboratory were -50°C/+100°C, being 100°C the regeneration temperature.

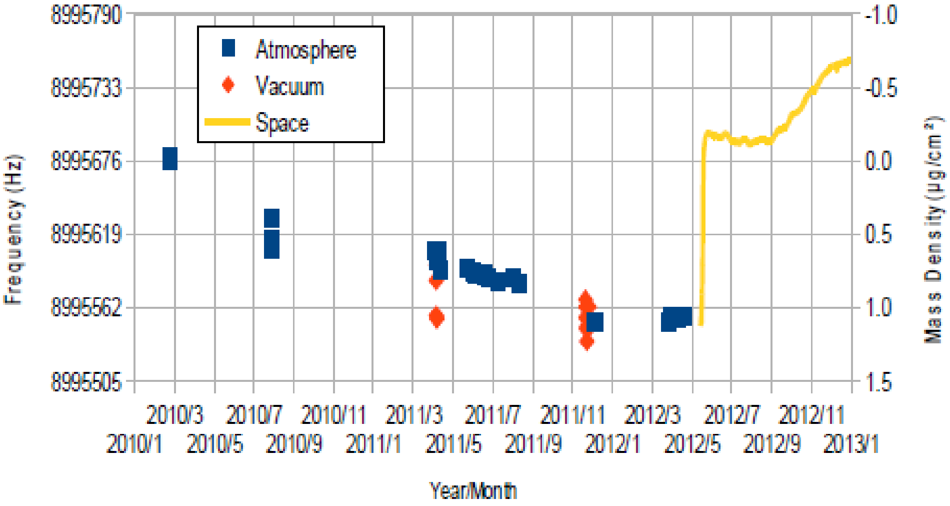
OGO-6 was inserted into a polar orbit and strong fluctuations of mass depositions of contaminants were measured during the satellite eclipse periods. As a matter of fact, the solar panel temperature was 72°C during the Sun exposition and a wide range of high and low volatile contamination outgassed on the QCMs. During maximum eclipse (30% in the Earth's shadow) the average solar panel temperature was 60°C and the contamination flux decreased significantly. Thus, comparing the contamination measurements and satellite eclipse, it can be said that the material deposited on the QCMs surfaces increased when the satellite was exposed to the Sun and decreased when the satellite is in the eclipse (since the lower outgassing flux from the solar panel did not balance the contaminant desorbed from the crystal surface). The maximum measured mass loading was 10^{-5} g/cm^2 and decreased to 9×10^{-6} g/cm^2 during the eclipse period. Nevertheless, the Reber's Neutral Mass Spectrometer revealed outgassing even during eclipse, when the QCMs measured a mass loss (McKeown 1973).

3.4.2 SDS-4

Small Demonstration Satellite-4 (SDS-4) was a follow-on technology demonstration mission of SDS-1 heritage, launched in 17th of May, 2012 on H-IIA Launch Vehicle and based on the SDS standard bus concept of JAXA (Japan Aerospace Exploration Agency). This was the first microsatellite with a mass of about 50 kg controlled by JAXA that aimed to demonstrate (https://earth.esa.int/web/eoportal/satellite-missions/s/sds-4):

i. the Space-based Automatic Identification System Experiment (SPAISE) whose objective was to demonstrate technologies of the future spaceborne AIS (Automatic Identification System) service by determining its performance via evaluation of on-orbit data and function; and
ii. Quartz Crystal Microbalance (QCM) device to measure the contamination of spacecraft environments during the whole microsatellite life cycle, e.g. the chemical thruster exhaust plumes and the AO environment; and
iii. Flat-plate heat pipe On-orbit Experiment (FOX) that intended to demonstrate and confirm the Flat-plate Heat Pipe (FHP) performance in a micro-gravity environment; and
iv. in-flight experiment of Space materials using THERME (IST) technologies that aimed to measure the solar absorbance and the degradation characteristics of the thermal control material and developed by a JAXA-CNES joint research project.

QCMs were provided by MEISEI ELECTRIC CO., LTD with the aim to monitor the chemical and electric thrusters exhaust plumes contamination and AO in high atmosphere. The microbalance, having a resonant frequency of 9 MHz and operative temperature between -40°C and 65°C, was placed in a metallic case with its electronics (measured results are provided in Fig.11). During the initial test phase (on ground) the QCM frequency decreased due to the contaminant deposition of 0.7 µg cm^{-2} during the component tests, and 0.3 µg cm^{-2} during the satellite test phase. Thus, 1 µg cm^{-2} of contaminants was observed during two years of ground activities (Nishiyama and Kuninaka 2014). In particular, temperature test, sinusoidal and random vibration tests, thermal vacuum test were executed and where the cleanness was not sufficient (e.g. during transfer and vibration tests) a plastic dust cover (non-flight item) was attached on the QCM to avoid excessive contamination. After shipment to the SDS-4 system in April 2011, the cover was removed in order to measure the actual contamination in the clean room environment that the satellite experienced. Successively, a rapid increase in frequency was recorded during the first week (May 17 – May 25, 2012, Fig.11) in orbit that mainly corresponded to the same frequency change (the mass loss rate increased from 0.22 to 0.88 μg cm^{-2} day^{-1}) obtained by on-ground contamination in two years (i.e. 1.1 μg cm^{-2}, equivalent to 5 Å thickness when the total thickness of the gold coating electrode is 2000 Å and the life time of the QCM is sufficiently long).



`Figure 11` (from Nakamura et al. 2013). The QCM frequency trend during the in ground assembly, the initial test and in space. In the first phases the frequency decreases because of contaminant deposition on the membrane. In space environment contaminants were removed and the frequency increase of 200 Hz.

The frequency increase was endorsed to the erosion of the gold electrode by the sputtering of fast neutral atoms and ions in the upper atmosphere or by corrosion of the carbon-rich contaminant deposited on the QCM surface induced by the chemical reaction with AO whose fluence was estimated as 2×10^{17} particles cm^{-2} (Nishiyama and Kuninaka 2014). The evaluated erosion (assuming a density of 1 g cm^{-3}) was 5.5×10^{-24} cm^{3} atom^{-1}, value near to the one of many organic materials such as polyimide, polyethylene, polyether-ether-keytone and carbon (Osborne et al. 2001).

The QCM had been successfully used for monitoring the spacecraft surface environment for seventeen months, providing a slow frequency increase. The frequency behaviour indicates that on SDS-4 satellite surface erosion is more dominant than contamination. Thus, no contaminant deposition was detected during SDS-4 mission time, differently on what observed in in-orbit measurements (operative phase of QCMs) performed in other space missions by using QCMs (Miura et al. 2013).

3.4.3 SMART-1

ESA SMART-1 mission (Small Mission for Advanced Research and Technologies), launched in 2003, was aimed to orbit the Moon for a nominal period of 6 months. SMART-1 was provided by Electric Propulsion Diagnostic Package (EPDP) and Spacecraft Potential and Electric fields and Dust Experiment (SPEDE) that monitored the Hall thruster plume interaction effects on the spacecraft (Gonzalez 2005). Both the experiments wanted to obtain information on the possible interaction of the thruster with the spacecraft subsystems. The Microbalance Assembly (MBA), included in the EPDP and used in this mission, was placed close to the solar cell sample and consisted in two matched crystals (10 MHz), one exposed to the outer space (sensing crystal) and the other inside the package (reference crystal). The goal was to monitor possible contaminant deposition of propellant ions during thrusters' operation (HET, Hall Effect Thruster) (Matticari et al. 2000), and to evaluate the erosion effect and redeposition of eroded materials (the impacted materials by the plasma) on the surrounding surfaces.

The 10 MHz QCMs were provided by QCM Research (MK17): the two clean crystals oscillated at the same frequency over a large temperature range with very small errors. The crystal temperature was measured by a RTD (PT1000), in order to monitor contamination at different temperatures. Once the deposition rate of contaminants was measured, the effect of contamination on thermo-optical and electrical parameters of different materials was retrieved (Tajmar et al. 2004).

The data coming from the solar cell and the QCMs demonstrates that the amount of eroded material was very low (i.e. the degradation of the cell was lower than expected), and this was confirmed by contamination measurements performed by other sensors on the same spacecraft (i.e. Solar Cell Assembly) (Gonzalez 2005).

3.4.4 LISA Pathfinder

Contamination & Deposition Diagnostics Assembly (CDA), comprising two physical sub-units (QCM and the Solar Cell Patch, SC) flown onboard the European Space Agency's (ESA) LISA Pathfinder, formerly called SMART-2, was launched in 2015. The mission aimed to test new technologies needed for the Laser Interferometer Space Antenna (LISA), ESA/NASA mission for gravitational waves detection.

During this mission, two Quartz Crystal Microbalances (QCMs) were installed close to the thruster, in order to measure contamination (deposition/erosion mass). One QCM was used to collect the metallic back sputtering due to ions impingement on the chamber walls while the second sensor collected the vapors of cesium by thruster of FEEP (Field Emission Electric Propulsion) propellant evaporation (Paita et al. 2012).

As in the case of SMART1 mission, the crystal package consisted of two matched quartz crystals: the sensing crystal (exposed to the outer space) and the reference crystal accommodated inside the package (its frequency was not affected by mass deposition). Crystals were equipped with a temperature sensor (PT1000) in order to monitor the crystal temperature (QCM Research, MK 17) while a heater was used to clean the quartz surface. The beating signal frequency range was between 1 kHz and 135 kHz with an accuracy of 0.1 Hz. The mass of each QCM was 25g, while the envelope had the dimensions of 21.7×21.7×26 mm. Ground test measured the needed power for steady state operation to be between 0.15 W and 2.5 W during the heating phase (Capacci et al. 2007). The scientific phase of the mission started on the 8th of March 2016 and in April 2016 ESA announced that LISA Pathfinder demonstrated that LISA mission was feasible. The thruster technologies were also validated as well, result that would be beneficial for future space projects. On June 2016, ESA presented the first results of two months of science operation on the developed technology for a space-based gravitational wave observation and quantum physics investigations it was possible to proceeds to the next step. Thus, LISA Pathfinder was deactivated on 30 June 2017 (http://sci.esa.int/lisa-pathfinder/59238-lisa-pathfinder-to-conclude-trailblazing-mission/). Measured data are still under processing and the results will be probably published after the publication of gravitational waves main findings.

3.4.5 DS-1

NASA's New Millennium Deep Space One (DS1), launched on October 24, 1998, was the first interplanetary spacecraft operating with solar electric propulsion. This mission was dedicated to test a payload with new technologies and to carry out a flyby of asteroid 9969 Braille and an encounter with Comet Borrely. The spacecraft used a Xenon ion thruster as primary propulsion system and the mission first objective was to validate the solar electric propulsion for interplanetary science mission, including the characterization of ion propulsion induced interaction and contaminations on the spacecraft payload.

Two matched QCMs (10 MHz) were integrated in Remote Sensor Unit (RSU) in order to characterize molybdenum contamination (a silvery-grey metal used with high resistance to high-temperatures) from the xenon ion engine and the contamination effects on the thermo-optical properties of sensitive surfaces. This was required since very thin coatings (even about few Angstroms) can produce significant variation in thermo-optical properties (solar absorbance and emittance) for materials used in spacecraft thermal control. Thus the QCMs (named QCM0 and QCM1) were used to monitor the accumulate of detectable amount of sputtered molybdenum atoms emitted in the general direction of the thrusters plume. The QCMs were selected by QCM Research with a very high sensitivity (<10 ng/cm^2): QCM0 pointed to the ion thrusters beam centerline (with an angle of 85°C) of NASA SEP Technology Applications Readiness (NSTAR), whereas QCM1 was shadowed from direct view of the Ion Propulsion System Engine. The long - term drift of the QCMs was not exceeding 50 ng cm^{-2} per month, which corresponded to a minimum detectable molybdenum deposit rate of 1 monolayer per year (Brinza et al. 2000).

During the launch phase, the beating frequency of QCM0 was increased of 187 Hz, providing an estimated mass deposit of 0.8 μg cm^{-2} (80 Å) accumulation due to the contaminants, which were removed when the DS1 was rotated versus the Sun. After a 240 h of flight, the QCMs were heated up to 75°C in order to bake-off volatile contamination: a little beat frequency variation (50 Hz) was obtained. Thus, QCM0 (aligned with thrusters) measured an average deposition of 141 Å per 1000 h (A kh^{-1}) deposition and QCM1 (not aligned with thrusters) measured 26 Å kh^{-1} deposition rate. These measurements gave an important result, confirming that the propellant (i.e. molybdenum) can travel upstream and deposit on sensitive surfaces, e.g. on optics (Buehler et al. 2004). Furthermore, the beat frequencies were sensitive to temperature change and solar illumination. As a matter of fact, a temperature variation of 60°C during the spacecraft maneuver caused a 100 Hz shift of frequency (due to the attitude control system and the sun-angle change), in accordance to what evidenced in previous literature studies.

After a longer period, about 2750 h, the QCM0 collected a total thickness of 250 Å of molybdenum from the launch through November 1999 whereas the QCM1 measured a deposition rate less than 5 Å kh^{-1} attributed to ionized molybdenum (Brinza et al. 2000). A correction for solar-illumination and temperature was not needed, since the effect on frequency was ($\Delta f < 50$Hz for $\Delta T < 60°$ C in the range +20°C to +80°C, and < 250Hz shadow to maximum illumination) less than those observed since launch (i.e. about 5000 Hz). Thermal effects were instead more important for QCM1 that measured frequency variation similar to what obtained from disturbances.

3.4.6 MSX

During the Midcourse Space Experiment (MSX) satellite (launched on April 24, 1996), five QCMs (four TQCM and one CQCM) provided on-orbit data to characterize the contamination levels around the spacecraft and inside the Cryogenic Spatial Infrared Imaging Telescope (SPIRIT III). CQCM was a Mark 16 type, provided by QCM Research, thermally coupled with the cryogenically cooled primary mirror of the SPIRIT III telescope whose components were cooled down to temperatures varying between 8 and 50 K.

The TQCM1 was maintained at -40°C and the others (TQCM2, TQCM3, TQCM4) at -50°C were mounted outside of the spacecraft and were expected to be cooler than all external contamination sources (Wood et al. 1996). The TQCMs purpose was to measure the silicone and organic contaminant flux on specific locations of the spacecraft. The CQCM was designed to operate at temperatures as low as 4 K and located adjacent to the primary mirror of SPIRIT III to monitor contamination of the mirrors and windows by condensed gases.

During the first few days after launch (Fig.12) there was some concern over a contaminant deposition, in particular for the identification of the deposited species (the water contamination would be a clear indication that the cover should be deployed without delay). A very little film accumulation occurred since the cover releasing (121 h and 166 h) and when the spacecraft was maneuvered in the Earth's shadow. This caused heating up of the telescope baffle and a redistribution of the gaseous adsorbed previously. For this reasons and due to condensation of 61 Å contamination thickness during the first seven days in orbit, two Thermogravimetric Analyses were performed on CQCM close to SPIRIT III primary mirror at 121st hour and 133rd hour MET that corresponded in:

1) CQCM was warmed up from 21.5 to 35 K at a rate of 1.5 K per minute, resulting in the frequency decrease from 2573 Hz to 2500 Hz with a peak of evaporation rate at 31K. This means that the

contaminant was not water because of the insignificant water vapor pressure at 34K (the data compared with the calibration confirmed that the most of condensed contaminant was oxygen).

2) CQCM was warmed up to 40 K at 1 K per minute: measured frequency decreased of about 20 Hz down to 2480 Hz was recorded.

At 166th hour, a new deposition of 163 Hz (72 Å thickness) occurred on CQCM (temperature at 21K) caused by the SPIRIT III one-minute door ejection. Thus, a new TGA cycle was performed and thanks to thermal-vacuum calibration performed at NASA Goddard, revealed that oxygen O_2 (caused by redistribution of previously condensed gaseous oxygen on the baffle within the telescope) and minor level of argon Ar were deposited (coming from the solid argon used for the cover coolant) (Wood et al., 1996, Wood et al., 2000).

After the cryogenic testing, two warm-up experiments (SPIRIT III End of Operations Test SECOT) were performed in order to accelerate the CQCM and SPIRIT III warm up and to determine how much H_2O deposited on the baffles near the entrance aperture. The spacecraft was maneuvered to allow heating due to the solar flux (14 heating pulses of 25 min duration, SECOT1) inside the telescope baffle (Fig.12, *Left*). Gases redistribution within the telescope occurred. During this operation, the CQCM was heated from 51 to 99K providing frequency increase of 450 Hz due to H_2O condensation (200 Å thickness film). Thus, in order to determine the species of condensed mass, a TGA was applied to CQCM with a warm-up rate of 2.5 K min^{-1}. The 200 Å thickness film started decreasing for temperatures larger than 150K and the entire film was removed at 165K, indicating that the matter was H_2O, coming from multilayer insulator (MLI) (Wood et al. 1998).
Another TGA was performed near the mission Day 140 (1997) in order to warm the CQCM up to near 300K (Fig.12, *Left*). This was done before the SECOT2 testing in order to complete the calibration of the QCM beat frequency vs. temperature. In the second set of heating pulses (16 heating pulses of 25 min duration, SECOT2) the CQCM temperature increased from 140 K up to 160K. During this time, the CQCM frequency increased from about 2600 Hz up to 3060 Hz, a value slightly higher than the deposition observed during SECOT1. Successively, no additional TGA cycles were needed because the CQCM temperature passed through the evaporation temperature up to the complete removal of the condensed film (mission Day 175).
By time period from telescope cool down prior to launch, until the SPIRIT III end of life, the CQCM frequency changed of only 30 Hz (13 Å) for the remainder of the Cryo period. Thus, the total deposition on CQCM was finally evaluated to be about 155 Å thickness (Wood et al. 2000).

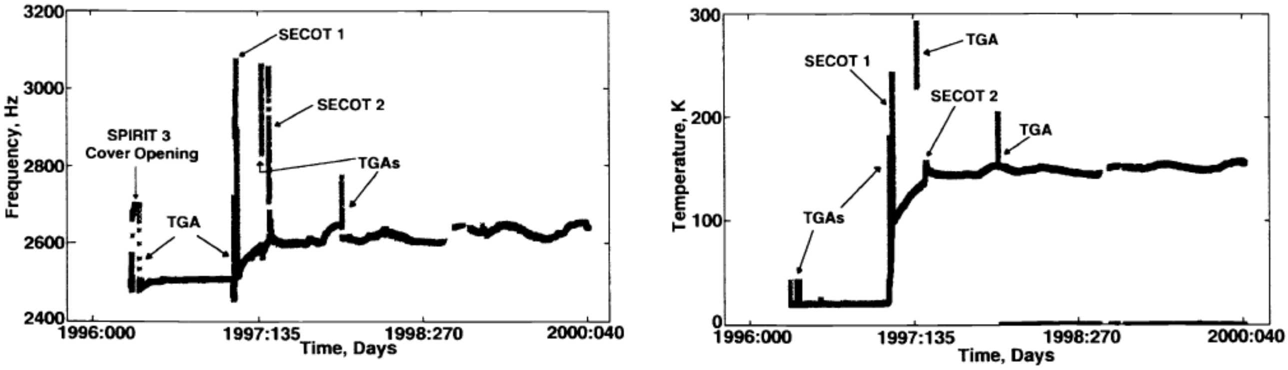
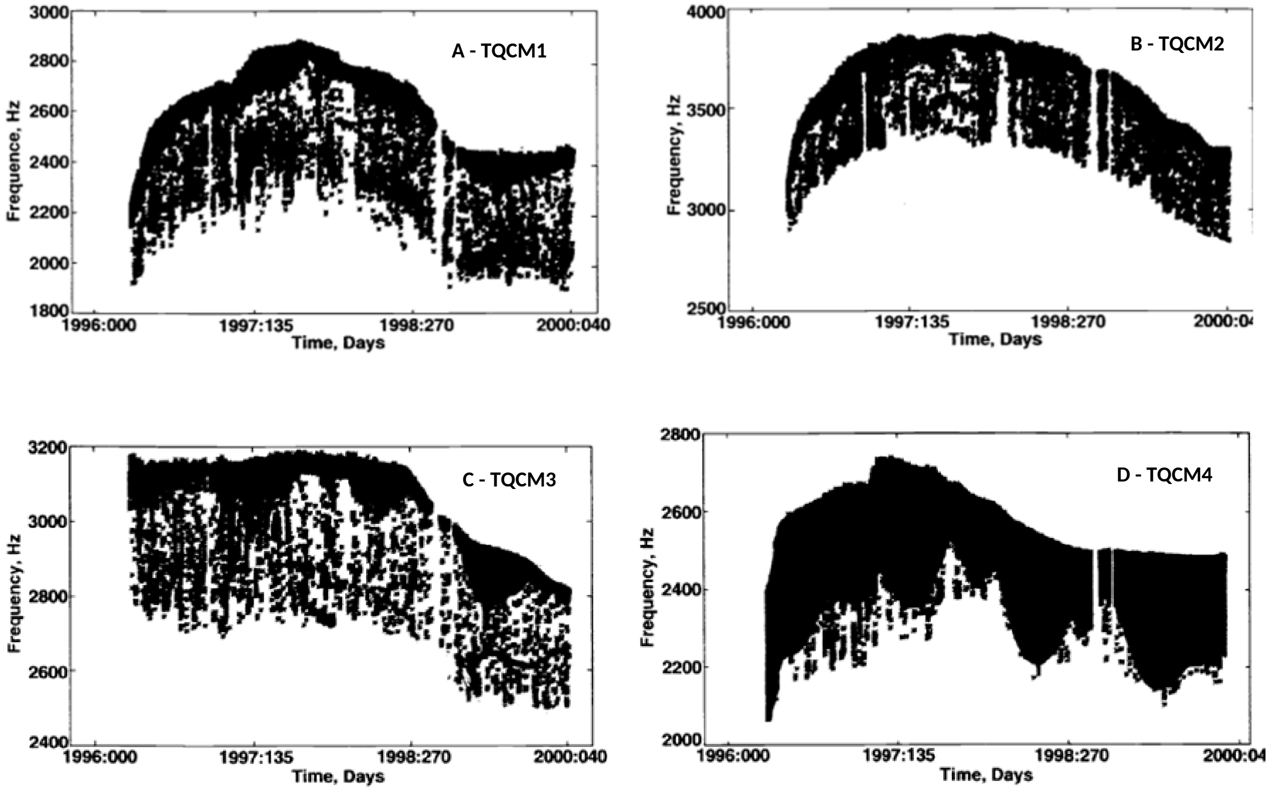


Figure 12 (from Wood et al. 2000). TGA curve in MSX: CQCM frequency versus time since launch (*Left*) and CQCM temperature versus time since launch (*Right*). SECOT indicates a series of heating pulses of 25 min duration to remove possible thin water layers deposited Oxygen/Argon on the telescope deflectors.

The TQCMs were mounted on individual radiators isolated from the main frame of the spacecraft to allow better thermal control. TQCMs temperatures (between -40 and -50 °C) were expected to be cooler than multilayer insulators, electronic boxes, and other non-cryogenically cooled surfaces in order to monitor many silicones and hydrocarbons outgassing. Because of the spacecraft rotation, the projected area of solar panel fell within the TQCMs' fields of view (FOVs). In particular, the TQCMs 1-2 had view factors that contained considerable area of the solar panels and spacecraft electronics module. The TQCM3 was positioned to view a direction where minimal contamination would be seen whereas TCMQ4 was mounted close to science instruments to obtain deposition rate on the sensitive surfaces.

Because of the TQCMs had the disadvantage of being sensitive to incident solar flux, many spikes were observed when the spacecraft was maneuvered out of park mode to other altitudes. In fact, negative frequency shifts of 300-450 Hz were measured for all the TQCMs during full or partial exposure to Sun. TQCM4 was the only one to measure different frequency change, i.e. 330 Hz in June and 240 Hz in October. This highlighted the possibility that the frequency decrease may be seasonal, or due to precession of the spacecraft orbit.

The frequency changes due to Sun exposition complicated the analysis. The problem was solved obtaining the deposition curves when the TQCMs were shadowed from the Sun (data points at the top of the curves) (Fig.13, D). TQCM1 and TQCM2 (RAM direction) showed the largest deposition rates due to solar panel (main sources of contaminants on MSX) on its FOV (Fig.13, A-B). The TQCM 3 (WAKE direction, the same of the science instruments), as expected, showed a low amount of deposition (i.e. only 42 Angstroms thickness) (Fig.13, C). For the TQCM4, under conditions of full Sun illumination, a frequency change of 330 Hz was observed. The frequency decrease with solar radiation was explained with the thermal stress generated in the quartz crystal by Solar exposure (Wood et al. 2000). TQCM1 and TQCM3 showed the same solar effect, and had the same orientation with respect to the Sun. The spikes were caused by the temperature difference between the two crystals, which increased significantly when the Sun radiation entered in the FOV of the microbalance.



`Figure` 13 (from Wood et al. 2000). A: facing in the (+Y, -X) direction and viewing the solar panels (ΔF_{sun}=300-450 Hz); B: TQCM2, facing into RAM direction (+Z) and also having the solar panel in its FOV (ΔF_{sun}=300-450 Hz); C: TQCM3, located in the WAKE direction (-Z, +Y, where minimal contamination would be seen) with only every small FOV of one solar panel, (ΔF_{sun}=300-450 Hz); D: TQCM4, facing in the same direction as the science instruments (+X), (ΔF_{sun}=330 Hz).

In addition, the frequency falls were also due to the reflected specular and scattered solar radiation from the solar panels and spacecraft blanketing. The solar radiation incident on the crystals showed two separate effects (Wood et al. 1998):

- negative shift in output frequency between 300 and 400 Hz when solar radiation is incident normally to the crystal; and
- solar UV component that solarizes the contaminant (silicon and organics) on external crystal such that during TGAs, only a small portion of the condensed mass evaporated.

The total thickness measured by the four TQCMs in the first 486 days in space (since launch) was 134, 144, 13, and 63 Å, respectively. The deposition rate on the TQCMs increased after the SPIRIT III telescope and Dewar warmed up at the end of Cryo period. The condensed contaminant film thickness increased for the first 400 to 600 days and then started decreasing between 62 and 93 % depending on spacecraft location with a thickness loss rate between 0.08 and 0.16 Åday^{-1}, depending on the TQCMs location.

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The film decreasing began after approximately 400 days in space for TQCM4, 550 days for TQCM1, 650 days for TQCM2 and 600 days for TQCM3 where the thickness film continued decreasing to points well below the initial ‘clean’ QCM level. TQCM 2 (pointed to ram direction) evidenced the greatest contaminant erosion rate with approximately 93 % of thickness eroded away while TQCMs 1 and 4 have had a thickness loss of 62 and 79 % (the thickness films remained constant at 50 and 13 Å), respectively (Wood et al. 2000).
An attempt to explain the TQCMs mass loss rate was made to correlate the measured values of AO erosion, although the AO at 900 km (MSX orbit), appears to be too low: 8.9×10^9 O atoms cm^{-2} s^{-1} in ram direction and basically zero in wake direction (Wood et al. 2000). Thus, the cause for this decrease (especially for TQCM3 pointed to wake direction) in thickness has not been firmly established.

In contrast to TGA data observed for the CQCM, two set of TGAs were performed on each of the four TQCMs (from -50 to +30°C and from -50°C to +60°C) showing very little (if any) change in frequency due to the crystal warm-up to 60°C. As a consequence, the contaminant, i.e. organics and silicones coming from material outgassing, was baked on. With respect to the earlier experiments, the microbalance on-board MSX showed an accuracy of the QCM temperature of ±0.25°C with a frequency resolution of ±2Hz, worse than LISA Pathfinder and SMART-1 (±0.1 Hz). The QCM regeneration was obtained by heating the crystal up to 60°C, a threshold lower than the DeepSpace1 (80°C) and OGO-6 (100°C).

4. Summary of QCMs results

QCM-based sensors were used in Space Shuttle flights and in satellite mission for the following goals:

- to monitor the contamination and the degradation near the scientific instruments, i.e. solar cell, telescope;
- to monitor the frequency trend, when the QCMs are exposed to full or partial sunlight;
- to estimate the erosion due to AO and AO fluence in the upper terrestrial atmosphere;
- to measure the contamination from the solar panels and induced from the Propulsion System of the spacecraft.

Different contaminant depositions were measured by QCMs:

- in the EIOM-3 experiment, an increase in weight and a mass deposition of 0.2 μg cm^{-2} in 424 days;
- in IECM, a mass deposition of 39 μg cm^{-2} (X direction), 16.4 μg cm^{-2} (-Y direction) 1.6 μg cm^{-2} (-X direction) and 1.2 μg cm^{-2} (-X and Z directions) in 244 hours;
- in the PIC experiment, a deposition of 2.56 μg cm^{-2} was measured on the MIR Station, 130-N Russian due to contaminants containing 7.5% of refractory materials and 80% of volatiles sublimating at 52°C;

and a mass deposition of 0.384 µg cm^{-2} was measured by the thrusters firings of the Orbiter PRCS (only 2% of refractory materials).

By means of SEM analyses, contaminants were found to have different origin: Carbon and Silicon particles from EIOM-3, Silicon, Aluminum, Magnesium, Zinc, Sulfur, Titanium and Chlorine (between 1 µm and 2 µm in size for aluminum and up to 370 µm for Zinc particles) from the IECM experiment and thruster firings particles from PIC. In the last case, measured damages were classified with small (<4 µm), medium (5-10 µm) and large craters (11-20 µm). In orbit, the contaminants were subjected to thermal cycles (controlled by a heater or a Peltier module) as in the MSX (from 20K to 40K for CQCM), IECM (from -60°C to 30°C) and PIC (20°C the average temperature) experiments, in order to allow the evaporation of the volatiles components. In the PIC experiment, regeneration process with temperature peak of 52 °C revealed desorption of most of materials. However, between 2 and 7% of the total mass were retained on the crystal, representing the more refractory materials. Anyway, the obtained results testified the possibility to clean the QCMs for the volatile components, opening the way for new QCM concept equipped with built-in heater to allow crystal regeneration. In order to remove from the measuring surface, the more refractory materials, higher temperature must be achieved (>200°C), changing the crystal material substrate, from quartz to GaPO4 (Palomba et al. 2018). This is nowadays under investigation as research projects, but no flight experiments have been documented yet.

In all the experiments, the Sun radiation on the crystal surface induced a frequency variation, ascribed to the temperature change. The frequency variation with temperature depends on the QCM configuration (SC or DC), crystal coating and on the incidence angle. As an instance, in MSX experiment, TQCMs showed sensitivity to incident solar flux, i.e. the frequency showed a negative shift (of about 240-450 Hz) depending on full or partial exposure to Sun conditions. On the other hand, during DS1 mission, QCMs were used to monitor the ion propulsion induced contamination for a total contaminant mass of 0.8 µg cm^{-2} that was successively removed when the DS1 was rotated to Sun.

For Space Shuttle missions, Mir experiments and satellite missions, 10 MHz and 15 MHz quartz crystal microbalances, having a mass sensitivity (in g/Hz × cm^2) of 1.56×10^{-9} (15 MHz, Faraday Lab. supplier), 4.43×10^{-9} (10 MHz, QCM Research) and 1.96×10^{-9} (15 MHz, QCM Research), respectively, were used.

The DC configuration was often preferred, except in some cases (SDS-4 satellite and MEDET experiment), in order to reduce the frequency changes caused by ambient temperature variations and hence to enhance the sensitivity of the measurement system. Actually, in MEDET experiment, SC configuration was used, even if another QCM was used as temperature sensor (to correct measured frequency). Summarizing the main findings of the flown experiments the following results can be listed:

- the total mass detected was between 0.2 $\mu g\ cm^{-2}$ and 58.2 $\mu g\ cm^{-2}$ for both volatile and refractory materials (IECM and EIOM3 experiments), and 0.193 $\mu g\ cm^{-2}$ for refractory materials, only (thrusters plume particles in PIC);
- the resolution frequency was ±1 Hz (IECM and REFLEX), ±2 Hz (PIC and MSX), 0.1 Hz (SMART1 and LISA Pathfinder), whereas the resolution in temperature is ±1°C (IECM and REFLEX), ±25°C for MSX and ±0.2°C for DS1;
- the maximum regeneration temperature was 100°C in OGO-6 while for the other missions was 75°C in DS1, 52°C in PIC, 60°C in MSX and 85°C in SDS-4 satellite mission;
- the QCM operative range temperature were subject to the sensor model and supplier: -50°C to +120°C for TQCMs (QCM Research) and -253°C for CQCMs (QCM Research), -50°C to +80°C for QCMs by Faraday Lab and -40 +65 °C the QCMs provided by MEISEI ELECTRIC CO.; and
- the output frequency of TQCMs is affected by the sensor orientation, direction, and distance from volatile sources, the solar irradiation or other reflecting surfaces (Earth, high albedo S/C parts). In particular, QCMs have the disadvantage of being very sensitive to incident solar flux. Frequency variations of 240-450 Hz were observed in MSX experiment, 500-800 Hz in REFLEX experiment and 50-300 Hz EOIM-3 experiment; this highlighted the need of correcting the measured frequency variation for the microbalance temperature (in order to solve the issue data acquired when the Sun is shadowed must be analysed, excluding data acquired during the solar pulses);
- the maximum source of contamination are the solar panels. In OGO-6 a large variation of deposited mass was observed from full Sun exposure to the eclipse period, showing contamination passing from $10^{-5}\ g/cm^2$ to $9 \times 10^{-6}\ g/cm^2$, respectively; and
- it has been demonstrated that the sensor regeneration can be obtained by means of Thermogravimetric and heating cycles with the desorption of the main volatile compounds.

Finally, QCMs sensors were used to measure the erosion phenomena by AO. In this case, used sensors were covered with proper substrate or coating (reactive with AO). As an instance, in SDS-4 satellite. the frequency variation (increasing of about 200 Hz) was measured in the launch phase due to the erosion of coating materials of the QCM surface while, in MEDET experiment, the carbon-coated QCM showed a lower frequency increase (about 60Hz) after two weeks, indicating a linear decrease of carbon mass.

In the satellite experiments, it was found that the main contamination sources are often generated by the Solar panels of the spacecraft. Indeed, the OGO-6 experiment measured a contamination of $10^{-5}\ g\ cm^{-2}$ during full exposition to Sun (solar panels temperature of 72°C) and $9\times10^{-6}\ g\ cm^{-2}$ during the maximum eclipse (30% in the Earth's shadow and Solar panels temperature of 60°C). The mass loss of contaminant was due to the fact that the lower flux from the solar panel did not balance the contaminant desorbed from the crystal surface.

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5. Conclusion and future perspectives

The Space Shuttle and Satellite push the use of QCM devices to understand and monitor the degradation due to contamination of scientific instruments, e.g. solar cells, telescopes, caused by outgassing phenomena in Space. These sensors are also used for on-ground measurement, i.e. to characterize the outgassing - deposition kinetics of materials in vacuum environment, where materials behavior can be studied (with Standard Test Methods used by NASA and ESA, i.e. ASTM-E1559 and ECSS-Q-TM-70-52A, respectively). Although some known weaknesses, such as the relative low range in mass deposition (hundreds of μg cm^{-2}), the difficult identification of specific compounds (or a mix of contaminants) causing contamination or condensation and the high sensitivity to temperature disturbance, it can be said that the QCM technology is mandatory choice for Space missions thanks to the following advantages:

- QCM required resources are limited, if one compares mass, volume and power budget of the common QCMs with the ones for scientific instrumentation;
- large operative temperature range: QCMs works within wide temperature range, from 20K to 393K, with extension to higher temperatures refractory material, regolith and debris of comet nuclei have to be studied;
- molecular contamination measurement: QCMs allow detection of contaminants (jeopardizing instruments performances) from outgassing processes in a large mass deposition range (from ng cm^{-2} to hundreds of μg cm^{-2}) in Space due to adhesives, plasticizers, tape, silicon and other polymers occur and potentially;
- particulate contamination measurement, from manufacturing, UV, thermal cycles, and thruster plume;
- atomic oxygen erosion (LEO orbits) evaluation on sensitive surfaces (e.g. optics, telescopes, mirrors, reflectors etc.): the QCMs require to be coated with a sacrificial layer, e.g. carbon; gold, zinc sulfide;
- monitoring degradation near the scientific instruments: the sensors allow evaluation of the deposited contaminants (thickness measurement) and related induced effects on the thermo-optical properties of sensitive surfaces;
- regeneration: deposited contaminants can be removed by heating the QCMs measuring surfaces; this allows increasing the lifetime of QCM sensors and identifying the volatiles and refractory contaminants.

Looking to the previous advantages, it can be understood why QCM technology is expected to be widely used in the next planned Space missions for contamination monitoring (and degradation of telescope mirrors, solar panel, detectors and other sensitive surfaces. As an instance, for ESA and NASA Solar Orbiter and Athena Missions, the contamination requirements would like to identify 300 ng cm^{-2} year^{-1}, 50 ppm (particulate) and 4 μg cm^{-2} (molecular) contamination, respectively. Fulfillment of these requirements can be assessed and validated by using QCM technology which demonstrated to be effective in well documented past flown missions.

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Besides, due to QCM-technologies improvement (e.g. high temperature accuracy and volatiles characterization) obtained during the recent years (Palomba et al. 2015), it will be also possible to characterize and distinguish volatiles and refractories contaminants, or pure compound in-situ by using TGA technique that can provide physical and thermochemical characterization of the analysed materials (Dirri et al. 2016).

Finally, the QCM technology is also currently used in non-space fields. In biomedical applications, appropriate active sites (e.g. Molecularly imprinted polymers method) deposited on QCM surfaces are used to detect proteins, amminoacids and antibiotics molecules (Lütfi Yola et al. 2014). Inficon, Gamry Instrument, NdK companies are nowadays using and developing QCMs with that purpose (Svedhem et al. 2003). QCMs can be used in terrestrial atmosphere studies. In the AEROSE experiment (Morris et al 2005), QCM technology showed capability to monitor dust storms (particle size detection between 0.15 μm and 10 μm during Sahara dust storm). QCM readings had been confirmed by independent measurements with SEM analysis (Effiong and Morris 2011).

QCMs are used in industrial and pharmaceutical fields, to monitor chemical/physical processes (Freedman et al. 2008), the vapour pressure and enthalpy of sublimation of (solid or liquid) substances or compounds (Dirri et al. 2016) or to monitor the bacterial attachment and growth on the crystal gold coated surface (QS 405-05-1, http://www.biolinscientific.com/publications/q-sense/).

The mechanical improvements and scientific objectives that QCM devices will reach during the next years will make it suitable instrument for contamination and degradation monitoring of spacecraft surfaces and sensitive payloads of future ESA and NASA space missions.

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- 2012 - 2013: **Master's degree in "Astronomy and Astrophysics"** at Sapienza University (Physics Department).
- 2014 - 2016: **PhD at Sapienza University**, Department of Information and Communication Technologies, **CV: "Radar and Remote Sensing".**

Professional Background:

- **2012 - 2013: IAPS-INAF collaborator**
- **2013 – 2014 : Research Felloship at IAPS-INAF**. Title: "Thermogravimetry analysis by means of Piezoelectric crystal microbalances" in the aim of MarcoPolo-R Mission (ESA Cosmic Vision)
- **2014 – 2016 : Research Felloship at IAPS-INAF** (Institute for Space Astrophysics and Planetology, Via del Fosso del Cavaliere, 100, 00133 Roma). Title: "Characterization of meteorites and organic materials by means of spectroscopy Vis-IR and Thermogravimetry techniques".

Awards:

The QCM device instrument developed during the CAM Project (developed and managed during the PhD course) has been awarded with: ***"Innovation Award"* at "WIRE16 Workshop** on Business, Research and Economics", organized and promoted by Frascati Scienza, from Frascati municipality and from European Commission and from **ESA-ESRIN (http://www.media.inaf.it/2016/06/20/wire16-microbilancia/).**

Relevant Experience:

1. ***VISTA Project*** (Volatile In-Situ Thermogravimeter Analyser). This project aims to develop a Thermogravimeter (a Piezoelectric Crystal Microbalance and the related Proximity Electronics) proposed for MarcoPolo-R Mission, to perform the in-situ measurements of volatile compounds in planetary environments.
   Position held: test manager for the test planned for VISTA Breadboard and data analysis manager, managing for design e trade-off activities for the Breadboard of the instrument and for the definition of the technical and scientific requirements.
2. ***CAM-ESA Project*** (Contamination Assessment Microbalance). This project has been developed in collaboration with Institute for Space Astrophysics and Planetology (IAPS-INAF), the Institute of Atmospheric Pollution Research (IIA-CNR), Politecnico di Milano and Kayser Italia and aims to monitor the contamination induced from spacecraft materials during in-orbit space missions for the next ESA payloads.
   Position held: Leader of Work Package "EM Test" and data analysis manager, collaborator for the design e trade-off activities for the Breadboard e Engineering Model of the instrument and for the definition of the technical and scientific requirements.
3. ***PRIN-INAF Project***. The project: "Composition and origin of Dark and Bright materials on Vesta", was developed in collaboration between Institute for Space Astrophysics and Planetology (IAPS-INAF), Università di Lecce and "Sapienza Università di Roma" and aimed to investigate the origin and composition of dark material deposits on Vesta and their relation with the bright deposits and the “average” material.

Position held: test manager for the laboratory analysis on planetary analogue samples (i.e. meteorites).

4. ***EUROCARES Project*** (European Curation of Astromaterials Returned from Exploration of Space): is a three year, multinational project, funded under the European Commission's Horizon2020 research programme to develop a roadmap for a European Sample Curation Facility (ESCF) for precious samples returned from Solar System exploration missions to asteroids, Mars, the Moon, and comets. the project is carried out in close cooperation between six different European countries and represent 14 different institutions: Natural History Museum, London, UK (NHM); National Institute for Astrophysics, Italy (INAF); Naturhistorisches Museum Wien, Vienna, Austria (NHMW); Muséum National d'Histoire Naturelle, Paris, France (MNHN); Centre de Biophysique Moléculaire, Orléans, France (CBM); Centre de Recherches Pétrographiques et Géochimiques, Nancy, France (CRPG); Thales Alenia Space UK, Bristol, UK (TAS); Open University, Milton Keynes, UK (OU) Deutsches Zentrum für Luft - und Raumfahrt, Cologne, Germany (DLR); University of Leicester, Leicester, UK (LEI); Public Health England, Soulsbury, UK (PHE); Dipartimento di Scienze della Terra, Università di Pisa, Italy (Pisa); Senckenberg Gesellschaft für Naturforschung, Frankfurt, Germany (SENCK); Université Libre de Bruxelles, Brussels, Belgium (ULB).

   ***Position held*:** collaborator for the design and materials definition of the Transportation Box used for samples transportation and containment of planetary samples.

Specialization sections:

- Space Missions – Planetology
- Astronomy and Astrophysics
- Themochemistry
- Spectroscopy
- Meteorites
- Astrobiology
- Instrumentation for Space Missions
- Management of Cryogenic and Thermo-Vacuum Systems.

Scientific papers:

1. **F. Dirri,** E. Palomba, A. Longobardo and E. Zampetti, *Piezoelectric Crystal Microbalance measurement of enthalpy of sublimation of* C_2*-*C_9 *dicarboxylic acids,* Atmospheric Measurement and Techniques, v.9, p.655-668, 2016.
2. **F. Dirri,** E. Palomba, A. Longobardo and E. Zampetti, *Measuring enthalpy of sublimation of volatiles by means of piezoelectric crystal microbalance*, Origin of Life and Evolution of Biospheres, 2016, DOI: 10.1007/s11084-016-9517-y
3. E. Palomba, A. Longobardo, **F. Dirri,** E. Zampetti, D. Biondi, B. Saggin, A. Bearzotti, A. Macagnano, *VISTA: a micro-thermogravimeter for investigation of volatile compounds on planetary environment*, Origin of Life and Evolution of Biospheres, v.46, p.273-281, 2016.
4. A. Longobardo, Palomba E., Capaccioni F., Ciarniello M., .. and **F. Dirri**, *Photometric behaviour of 67P/Churyumov-Gerasimenko and analysis of its pre-perihelion diurnal variations*, Monthly Notices of the Royal Astronomical Society, Vol. 469, Issue Suppl_2, p.S346-S356, July 2017.

Proceedings:

1. **F. Dirri**, E. Palomba, A. Longobardo, E. Zampetti, D. Biondi, A. Boccaccini, S. Pantalei and A. Zinzi, *Measuring enthalpy of sublimation of volatiles by means of micro-thermogravimetry for the study of the water and organics in planetary environments*, MSAIS, v.26, p.133, 2014.
2. **F. Dirri**, E. Palomba, A. Longobardo, D. Biondi, A. Boccaccini, B. Saggin, D. Scaccabarozzi, E. Zampetti, *QCM-based sensors for volatile organic compounds characterization*, IEEE Xplore Digital Library, 2017.
3. B. Saggin, D. Scaccabarozzi, M. Magni, M. Tarabini, E. Palomba, A. Longobardo, **F. Dirri**, E. Zampetti, *Assessment of TEC suitability for a low temperature QCM*, IEEE Xplore Digital Library, 2017.

Abstract:

1. **F. Dirri**, M. Ferrari, E. Palomba, A. Longobardo, S. Stefani, A. Rotundi, A. Galiano and L. Nardi, *FT-IR and μ-IR analysis of Carbonaceous Chondrite meteorites characterization as possible analogue of next sample returned materials*, European Planetary Science Congress 2017, held 17-22 September 2017 in Riga, Latvia, 851.
2. M. Ferrari, **F. Dirri**, E. Palomba, S. Stefani, A. Longobardo and A. Rotundi, *FT-IR and μ-IR characterization of HED meteorites in relation to infrared spectra of Vesta-like asteroids*, European Planetary Science Congress 2017, held 17-22 September 2017 in Riga, Latvia, 859.
3. **F. Dirri**, E. Palomba, M. Ferrari, A. Longobardo, A. Rotundi, *A combined FE-SEM/EDS and μ-IR analysis of CM, CI and CV chondrites for next sample return missions*, European Astrobiology Network Association, 2016.
4. **F. Dirri**, E. Palomba, M. Ferrari, A. Longobardo, A. Rotundi, *A combined FE-SEM/EDS and μ-IR analysis of Carbonaceous Chondrites, analogue of the next returned asteroid samples*, 48th Division for Planetary Sciences - 11th European Planetary Science Congress 2016.
5. M. Ferrari, **F. Dirri**, E. Palomba, A. Longobardo, A. Rotundi, *FE-SEM/EDS and μ-IR combined analysis of HED meteorites in relation to infrared spectra of Vesta-like asteroids*, 48th Division for Planetary Sciences - 11th European Planetary Science Congress, 2016.
4. Longobardo, E. Palomba, F. Capaccioni, M. Ciarniello, F. Tosi, S. Mottola, L. Moroz, G. Filacchione, A. Raponi, E. Quirico, A. Zinzi, M.T. Capria, D. Bockelee-Morvan, S. Erard, C. Leyrat, G. Rinaldi and **F. Dirri**, *Photometry as indicator of comets' surface roughness*, European Planetary Science Congress 2017, held 17-22 September 2017 in Riga, Latvia, 781
5. **F. Dirri**, A. Longobardo, E. Palomba, A. Hutzler and L. Ferrière, *Basic design of sample container for transport of extraterrestrial samples*, European Planetary Science Congress 2017, held 17-22 September 2017 in Riga, Latvia, 811.
6. A. Galiano, E. Palomba, A. Longobardo, A. Zinzi, M.C. De Sanctis, A. Raponi, F.G. Carrozzo, M. Ciarniello and **F. Dirri**, *Continuum definition for Ceres absorption bands at 3.1, 3.4 and 4.0 μm*, European Planetary Science Congress 2017, held 17-22 September 2017 in Riga, Latvia, 704.
7. L. Nardi, E. Palomba, A. Longobardo, A. Galiano and **F. Dirri**, *Deriving global Olivine distribution on Hayabusa's target (25143) Itokawa using Near-Infrared Spectrometer data*, European Planetary Science Congress 2017, held 17-22 September 2017 in Riga, Latvia, 145.
8. E. Palomba, **F. Dirri,** A. Longobardo, A. Galiano, D. Biondi, A. Boccaccini, E. Zampetti, B. Saggin, D. Scaccabarozzi, *VISTA: a miniaturized thermogravimeter to detect planetary dust and volatiles, 3rd International Workshop on Instrumentation for Planetary Missions*, held 24-27 October 2016 in Pasadena, CA, USA, 4010.
9. Palomba E., Longobardo A., **Dirri F.,** Biondi D., Boccaccini A., Galiano A., Zampetti E., Saggin B., Scaccabarozzi D., *VISTA, a thermogravimeter to measure dust and volatile from Dydimos*, AIM Science Meeting, 2016.
10. Longobardo A., **Dirri F.,** Palomba E., Berthoud L., Holt J., Pottage T., Bridges J., Vrublevskis J., Bennett A., Smith C., Russell S., *Basic requirements for packaging and transporting returned extra terrestrial samples from landing sites to curation facility*, European Astrobiology Network Association, 2016.
11. Palomba E., **Dirri F.,** Longobardo A., Biondi D., Saggin B., Scaccabarozzi D., Zampetti E., *CAM: Contamination Assessment Microbalance,* Metrology for Aerospace 2016.
12. Palomba E., **Dirri F.,** Longobardo A., Galiano A., Biondi D., Boccaccini A., Zampetti E., Saggin B., Scaccabarozzi D., *VISTA: a miniaturized thermogravimeter to detect planetary dust and volatiles*, 3rd International Workshop on Instrumentation for Planetary Missions 2016.
13. **Dirri F.**, Palomba E., Longobardo A., Zampetti E., Biondi D., Boccaccini A., *Micro-thermogravimetry: a miniaturized technique for in-situ measurement of volatiles in planetary environments*, XII Congresso Nazionale di Scienze Planetarie, 2015.
14. Palomba E., Longobardo A., **Dirri F.**, Biondi D., Bearzotti A., Zampetti E., Macagnano A., Saggin B., Scaccabarozzi D., *Characterization of lunar levitating dust and measurement of volatiles: the MOVIDA instrument,* European Lunar Symposium, 2015.
15. Palomba E., Longobardo A., **Dirri F.**, Biondi D., Boccaccini A., Saggin B., Scaccabarozzi D., Zampetti E., Macagnano A., Bearzotti A., *VISTA, a light and cheap sensor to measure volatile amount and dust deposition*, 11th Low-Cost Planetary Mission Conference, 2015.
16. **Dirri F.**, Palomba E., Longobardo A., Zampetti E., Biondi D., Boccaccini A., *Micro-thermogravimetry for planetary in-situ measurement*, European Planetary Science Congress, 413, 2014.
17. Palomba E., Zampetti E., Longobardo A., Biondi D., Saggin B., Boccaccini A., **Dirri F.**, *VISTA: a micro-Thermogravimeter to analyze condensable species in planetary atmospheres*, 40th COSPAR Scientific Assembly, 2014.
18. Palomba E., Longobardo A., **Dirri F.**, Zampetti E., Biondi D., Boccaccini A., Saggin B., Scaccabarozzi D., Bearzotti A., *VISTA, a micro-Thermogravimeter to measure water and organics content in planetary environments*, International Workshop on Instrumentation for Planetary Missions, 2014.
19. Longobardo A., Palomba E., **Dirri F.,** Biondi D., Zampetti E., Saggin B., Scaccabarozzi D., Bearzotti A., Macagnano A., *Measuring volatile content and charging processes of lunar dust: the MOVIDA μ-Thermogravimeter*, European Planetary Science Congress, 2014.