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Electrical properties of tholins and derived constraints on the Huygens landing site composition at the surface of Titan

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Key Points:

- The complex permittivity of tholins was measured in laboratory at low frequencies and low temperatures
- By comparison with measurements from Cassini/Huygens, constraints on the composition of the Huygens Landing Site are derived
- There is evidence for the presence of a conductive superficial layer at the Huygens Landing Site

Abstract

In 2005, the complex permittivity of the surface of Saturn's moon Titan was measured by the PWA-MIP/HASI (Permittivity Wave Altimetry-Mutual Impedance Probe/Huygens Atmospheric Structure Instrument) experiment on board the Huygens probe. The analysis of these measurements was recently refined but could not be interpreted in terms of composition due to the lack of knowledge on the low-frequency/low-temperature electrical properties of Titan's organic material, a likely key ingredient of the surface composition. In order to fill that gap, we developed a dedicated measurement bench and investigated the complex permittivity of analogs of Titan's organic aerosols called "tholins". These laboratory measurements, together with those performed in the microwave domain, are then used to derive constraints on the composition of Titan's first meter below the surface based on both the PWA-MIP/HASI and the Cassini Radar observations. Assuming a ternary mixture of water-ice, tholin-like dust and pores (filled or not with liquid methane), we find that at least 10% of water ice and 15% of porosity are required to explain observations. On the other hand, there should be at most 50-60% of organic dust. PWA-MIP/HASI measurements also suggest the presence of a thin conductive superficial layer at the Huygens landing site. Using accurate numerical simulations, we put constraints on the electrical conductivity of this layer as a function of its thickness (e.g., in the range 7-40 nS/m for a 7-mm thick layer). Potential candidates for the composition of this layer are discussed.

1 Introduction

On January 14, 2005, the Huygens probe [Lebreton and Matson, 2004], part of the Cassini/Huygens mission (NASA/ESA/ASI), landed on the surface of Titan, Saturn's biggest moon [Lebreton *et al.*, 2005]. After two hours and a half of descent, the probe touched a solid and possibly wet ground [Zarnecki *et al.*, 2005; Atkinson *et al.*, 2010] at a latitude of 10.3 °S and a longitude of 192.4°W [Karkoschka *et al.*, 2007]. While the measurements performed by the instruments on board Huygens cannot be regarded as representative of the entire surface of Titan, they do provide an important ground truth for the understanding of the observations of the Cassini orbiter or Earth-based telescopes.

Among the instruments on board the Huygens probe, a Mutual Impedance Probe (MIP), called PWA-MIP/HASI (Permittivity Wave Altimetry-Mutual Impedance Probe/Huygens Atmospheric Structure Instrument), measured for the first time the low-frequency (namely at 45, 90 and 360 Hz) electrical properties (i.e., the dielectric constant and electrical conductivity) of the first meter of Titan's surface [Fulchignoni *et al.*, 2005]. Hamelin *et al.* [2016] recently refined the analysis of the PWA-MIP/HASI observations, accounting for new insights on the final resting position of the Huygens capsule [Schröder *et al.*, 2012]. They inferred a dielectric constant of 2.5 ± 0.3 and a conductivity of 1.2 ± 0.6 nS/m at 45 Hz, values which are in agreement with previously published results but with much more reliable error bars. Following Grard *et al.* [2006], Hamelin *et al.* [2016] also reported that a sudden change in the electrical properties of the ground, namely a drop of its electrical conductivity, was recorded about 11 min after the Huygens landing. Several scenarios have been advanced to explain this event but more information on the electrical properties of materials relevant to Titan's surface at PWA-MIP/HASI frequencies are required to better understand PWA-MIP/HASI results in terms of near-surface composition and to conclude on the most plausible scenario for the observed sudden change in conductivity.

Prior to the Cassini mission, the composition of Titan's surface was thought to be that of its bulk crust i.e., dominated by water ice [Tobie *et al.*, 2005]. This was supported by the detection of water ice by Griffith *et al.* [2003] from telescope infrared spectroscopy measurements. However, since then, Cassini-Huygens observations have shown that water ice is only exposed at the surface of Titan at isolated locations including interdune corridors [Barnes *et al.*, 2008; Le Gall *et al.*, 2011] and crater rims [Janssen *et al.*, 2016]. In-

69 stead, the surface seems to be covered by a layer of organic materials, by-products of the
70 intense photochemistry activity of Titan's atmosphere [Clark *et al.*, 2010; Janssen *et al.*,
71 2016].

72 The atmosphere of Titan is indeed the host of a complex photochemistry that pro-
73 duces a wealth of solid organic matter (or aerosols) by dissociation (mainly by solar UV
74 rays) and recombination of the molecules N₂ and CH₄ [Lorenz and Mitton, 2002; Waite
75 *et al.*, 2007]. The heaviest of these aerosols are eventually deposited onto the surface, pro-
76 gressively forming a thick sedimentary layer of organics. With time, surface processes
77 (e.g., aeolian/pluvial/fluvial erosion, impacts, etc...) erode this layer and/or mix organics
78 with water ice (see Lopes *et al.* [2010] for a review).

79 The present work aims at inferring new constraints on Titan's near-surface composi-
80 tion (in particular on its water-ice/organic mixture) from the electrical measurements made
81 by PWA-MIP/HASI by comparison with laboratory measurements. While the electrical
82 properties of water ice are well known [Mattei *et al.*, 2014], those of Titan's aerosols have
83 never been measured at low frequencies in laboratory. In this paper, we present the mea-
84 surement bench that we have developed to fill this gap. Measurements were performed
85 on analogs of Titan's aerosols called "tholins" at a wide range of temperatures from room
86 temperature down to almost 90 K. Measurements made at Titan's surface temperature
87 (93.65 ± 0.25 K [Fulchignoni *et al.*, 2005]) were then used to better understand the impli-
88 cations of the PWA-MIP/HASI observations at the Huygens landing site (hereafter referred
89 as to HLS).

90 2 Materials and Methods

91 2.1 Productions of tholins

92 The term "tholins" was introduced by Sagan and Khare [1979] to name the "brown,
93 sometimes sticky, residue" they produced in laboratory at Cornell University by irradi-
94 ating with various sources of energy a mixture of the cosmically abundant gases CH₄,
95 C₂H₆, NH₃, H₂O, HCHO, and H₂S. The definition was later expanded to include many
96 other components produced from different mixtures and even by irradiation of ices. It now
97 seems that tholin-like materials are present in many bodies in the Solar System: on Pluto
98 [Grundy *et al.*, 2016], Charon [Grundy *et al.*, 2016], comets [McDonald *et al.*, 1996; Stern
99 *et al.*, 2015], Triton [McDonald *et al.*, 1994] and, of course, Titan [Sagan *et al.*, 1993].

100 Several set ups have been developed to synthesize and study analogs of planetary
101 organic aerosols in laboratory (e.g., [Szopa *et al.*, 2006] [Cable *et al.*, 2012]). In particular,
102 the PAMPRE (French acronym for Production d'Aérosols en Microgravité par Plasma RE-
103 actifs – Aerosols Production in Microgravity by Reactive Plasma, [Szopa *et al.*, 2006]) ex-
104 periment developed at LATMOS has been designed to reproduce the complex photochem-
105 istry of Titan's atmosphere. PAMPRE simulates the UV photolysis of N₂ and CH₄ and the
106 induced photochemistry using a Capacitively Coupled Plasma (RF-CCP) discharge. This
107 discharge is applied to a mixture of N₂ and CH₄ with a N₂/CH₄ ratio in the range 90/10
108 to 99/1, consistent with Titan's atmosphere composition at different altitudes [Waite *et al.*,
109 2007]. Inelastic electron impacts dissociate N₂ and CH₄ [Szopa *et al.*, 2006] and the re-
110 sulting ions, neutral atoms and radicals recombine to form solid particles [Carrasco *et al.*,
111 2012]. The advantage of using a capacitive coupled RF plasma discharge is that the pro-
112 duced particles are in levitation between the two electrodes due to electrostatic forces and
113 only deposit once they are heavy enough. This prevents them from interacting with the
114 reactor walls that could act like a catalyst [Szopa *et al.*, 2006].

115 The PAMPRE-produced tholins are small spherical particles with a mean diame-
116 ter between 0.093 and 1.070 μm [Hadamcik *et al.*, 2009]; they are regarded as possible
117 analogs of Titan's organic aerosols. They form aggregates which can be observed micro-

118 scopically and have the macroscopic appearance of an orange powder (see Figure A.1) in
119 agreement with the color of Titan's haze.

120 2.2 The PAP measurement bench

121 The central instrument of the PAP (French acronym for Permittivité d'Analogues
122 Planétaires, permittivity of planetary analogs) measurement bench developed at LATMOS
123 is a spectral analyzer (Solartron Modulab Material Test System©). The spectral analyzer
124 uses a dipole system to generate an alternating current at frequencies in the range 1 Hz
125 - 100 kHz between two electrodes separated by the cylindrical sample of material to be
126 analyzed. The current and potential on the electrodes are then measured giving access to
127 the complex impedance of the sample and thereby to its complex permittivity i.e., both its
128 dielectric constant and electrical conductivity . The PAP electrodes are cylindrical with a
129 radius of 10 mm and a height of 8 mm. An additional module was installed in order to
130 measure currents down to the femto-Ampere which is necessary for materials with low
131 dielectric constant and/or conductivity.

132 The PAP measurement bench also includes:

- 133 1. A mechanical press to produce samples of varying bulk density. Samples are shaped
134 as cylinder pellets of 10 mm diameter with a height of 1 mm. A pressure of up to
135 8.8×10^8 Pa (maximum tonnage of 7 tons) can be applied to them.
- 136 2. A sample holder in which the electrodes and the sample are placed.
- 137 3. A pump to create vacuum (minimum 10^{-2} mbar) in the sample holder in order to
138 prevent contamination by water ice (formed by condensation of the water in the air)
139 of the sample when the temperature drops.
- 140 4. A cryostat to perform measurements at low temperatures. Cryogenic temperatures
141 are reached by passive cooling, filling up with liquid nitrogen the reservoir in which
142 the sample holder is placed. The temperature is recorded on both electrodes by
143 PT100 temperature sensors. The temperatures recorded on the two electrodes are
144 very close and we use the average of these two measurements to estimate the sam-
145 ple temperature. The lowest achievable temperature with this device is about 94 K,
146 i.e. Titan's surface temperature at the HLS, and is obtained after ≈ 1 hr of cooling.
147 After about 10 hrs all liquid nitrogen is evaporated and the temperature increases
148 back to room temperature within about an additional 10 hrs. The temperature range
149 for our measurements is therefore from 94 K up to room temperature.

150 The PAP set-up is designed to measure the complex permittivity of solid samples.
151 In a harmonic regime and using complex notation, it is common to refer to the relative
152 complex permittivity of the medium (i.e., relative to that of vacuum $\epsilon_0 = 8.854 \times 10^{-12}$
153 F/m) defined for fields and potentials in $\exp(j\omega t)$ as follows:

$$154 \epsilon_r = \epsilon_r' - j\epsilon_r'' \quad (1)$$

155 The real part of the permittivity ϵ_r' (hereafter referred to as the dielectric constant)
156 describes the polarizability of a material when an electrical field is applied. Its imaginary
157 part ϵ_r'' is related to the electrical effective conductivity σ as follows: $\epsilon_r'' = \sigma/2\pi f\epsilon_0$ with
158 f the working frequency. We note that while pure dielectric materials have, by definition,
159 a zero true conductivity (i.e., no free charge), polarization mechanisms induce the heat
160 dissipation of electrical energy, which gives rise to a non-null effective conductivity.

161 The derivation of the complex permittivity from PAP measurements is described in
162 Appendix A.

2.3 Description of the samples

The tholin samples were produced by the PAMPRE experiment for 3 different compositions of the initial gas mixture: 2%, 5% and 8% of CH₄. We investigated 15 samples i.e., 5 per composition totaling up to 300 hours of measurements most of which could be done unattended.

The material density of the tholins was measured using a helium pycnometer (Upsc-1200e-V5.04) which evaluates the volume occupied by a given sample with a known mass in a calibrated chamber by inserting helium gas in the chamber. The measured material densities (i.e. zero-porosity densities) are: $\rho_{tholins2\%} = 1.45 \pm 0.02$, $\rho_{tholins5\%} = 1.44 \pm 0.03$ and $\rho_{tholins8\%} = 1.34 \pm 0.03$. The porosity of the compressed samples measured with PAP can be readily inferred from these material densities. We find that the porosity of our samples is in the range 10-40%. Our experimental set up cannot produce samples with porosity out of this range. Samples with porosity >40% are too loose to be handled and placed in the sample holder. On the other hand, the mechanical press cannot compress further the samples. Of note, the material density values we found are consistent with those published by *Imanaka et al.* [2012] ($\rho_{tholins10\%} = 1.35 \pm 0.05$) but higher than those published by *Trainer et al.* [2006] ($\rho_{tholins} = 0.8 \pm 0.05$) and *Hörst and Tolbert* [2013] ($\rho_{tholins} \approx 0.5 - 1.15$). The difference in the experimental setup used to produce the tholins prevents a direct comparison although it seems that UV irradiation of CH₄ produces lower density tholins.

Futhermore, the composition of the initial gas mixture has an effect on the optical properties of the tholins; the higher the methane content the darker they appear. Additionally, the 2% samples were found to be less sticky and making pellets out of them proved to be more difficult than for the other compositions.

3 Complex permittivity of tholins

3.1 Effect of porosity

Figure A.2 shows the effect of porosity on the samples electrical properties. Overall and as expected, both the real and the imaginary parts of the permittivity decrease when porosity increases, vacuum having the lowest possible values of dielectric constant and conductivity (namely $\epsilon'_{r0} = 1$ and $\epsilon''_{r0} = 0$).

We use these measurements to determine the complex permittivity of the bulk tholins (i.e., with no porosity). This can be achieved by using a mixing law to "correct" the electrical properties of the investigated tholin samples for the contribution of vacuum. More specifically, we use the Maxwell-Garnett law [*Garnett*, 1904], which is the mixing law that best fits the data points presented in Figure A.2. This law relates the complex permittivity of the sample to its porosity p as follows:

$$\epsilon_{rsample} = \epsilon_{rm} + 3p\epsilon_{rm} \frac{1 - \epsilon_{rm}}{1 + 2\epsilon_{rm} - p(1 - \epsilon_{rm})} \quad (2)$$

where ϵ_{rm} is the bulk permittivity of tholins that can then be estimated by solving the second-degree equation:

$$2(p - 1)\epsilon_{rm}^2(p\epsilon_{rsample} - 2p + 2\epsilon_{rm} - 1)\epsilon_{rm} + \epsilon_{rsample}(1 - p) = 0 \quad (3)$$

The Maxwell-Garnett mixing law assumes that the void (spherical) pores (valid for $p < 0.5$) are smaller than the wavelength (300 m) which is readily achieved in our case. For example, at 94 K, 100 Hz and for a 5% methane composition the corrected complex permittivity is 4.5-j0.02.

3.2 Effect of frequency and temperature

Figure A.3 shows the complex permittivity of bulk tholins (i.e., once the correction described in section 3.1 has been applied) as a function of frequency and temperature for the three considered initial gas mixture compositions. The continuous lines and the shaded areas respectively represent the average and the standard deviation (at 2σ) of the 5 samples measured per composition.

As expected, the dielectric constant increases with a decreasing frequency because polarization mechanisms have more time to take place when the applied electric field is slowly oscillating. Also the frequency dependence tends to disappear and the dielectric constant decreases when the temperature decreases i.e., when charge carriers become too slow to follow the applied electric field oscillations whether these oscillations are rapid or not. In particular, at Titan's surface temperature the dielectric constant seems to have reached its static limit.

The imaginary part of the complex permittivity displays a maximum at a frequency that moves towards lower values when the temperature decreases (1000 Hz at 220 K and 1 Hz at 170 K). The relaxation process at play may be a Maxwell-Wagner effect (i.e., interfacial polarization between the pores and the tholin matrix). At very low temperatures (in particular at 94 K), the relaxation peak is not visible anymore. Like for the real part, the imaginary part of the permittivity decreases with decreasing temperatures.

3.3 Effect of composition

We note a significant change in the electrical properties as a function of the composition of the gas mixture (i.e., the N_2/CH_4 ratio) from which they have been produced. The "5%-tholins" have the largest dielectric constant while the "8%-tholins" have the smallest (Figure A.4). This is true for all frequencies in the range 1 Hz-100 kHz.

For temperature in the range 125-225 K, the imaginary part of the permittivity of the tholins increases with an increasing methane proportion in the PAMPRE gas mixture. Outside this temperature range, the "2%-tholins" methane proportion still has the smallest imaginary part of the permittivity but the "5% tholins" has the largest (see Figure A.4). This is true for all frequencies in the range 1 Hz-100 kHz.

At 94 K and at a given frequency the dielectric constant varies by 0.5 and the imaginary part of the permittivity by 0.02 between the 3 studied compositions. This variation is larger than the accuracy of the spectral analyzer and higher than the dispersion of the measurements performed on multiple samples which gives us, in theory, the ability to distinguish between the different compositions.

Tholins show very low concentration of polycyclic aromatic hydrocarbons [Derenne *et al.*, 2012; Mahjoub *et al.*, 2016], therefore, the differences observed in the electrical properties are probably not due to the presence of aromatic components. Mahjoub *et al.* [2012] investigate the optical indices of tholins as a function of the methane percentage used in the initial gas mixture. They find that the 2% tholins are far more absorbant in the UV-visible than the 8% tholins and explain this difference by the quantity of nitrogen incorporated in the tholins, primarily in amines, which was found to be higher at low methane fraction in the initial gas. In amines, the nitrogen has a non-binding electrical doublet which results in a higher dielectric constant. This could explain the differences between the 8% and 5% tholins but the fact that the 2% tholins have a lower dielectric constant than the 5% suggests that additional unknown mechanisms influence the electrical properties.

The measured dielectric constant of tholins at low frequency is relatively close but different from that of water ice (3.15 at cryogenic temperatures [Mattei *et al.*, 2014]) or of Martian analog JSC-Mars-1 (2.0-2.5 at 220 K [Simões *et al.*, 2004]). Furthermore, at

256 low frequencies most rocky materials present on the Earth have a dielectric constant in the
257 range 3.4 (dry sandy soil [Clark, 1966]) - 13.0 (sandstone [Clark, 1966]).

258 3.4 Dielectric relaxation model for tholins

259 One of the most commonly used models to represent the frequency dependence of
260 the electrical properties of material is the Cole-Cole model with conduction [Cole and
261 Cole, 1941]:

$$262 \epsilon_r(f, T) = \epsilon_\infty(T) + \frac{\epsilon_s(T) - \epsilon_\infty(T)}{1 + (j2\pi f\tau(T))^{1-\alpha}} - j \frac{\sigma_s}{2\pi f \epsilon_0} \quad (4)$$

263 where ϵ_∞ is the relative high-frequency limit permittivity, ϵ_s the static (low-frequency
264 limit) relative permittivity, τ the relaxation time in seconds, σ_s the static conductivity and
265 α an exponent representing the broadness of the relaxation transition. It is reduced to the
266 Debye equation when $\alpha = 0$.

267 Figure A.5 shows the Cole-Cole model best fitting to our measurements in the com-
268 plex plane (plotted with different scales for ϵ'_r and ϵ''_r) at a temperature of 94 K for tholins
269 obtained with 5% of methane. The best-fit parameters are: $\epsilon_s = 4.24$, $\epsilon_\infty = 4.53$, $\tau =$
270 2.0×10^{-4} s, $\alpha = 0.84$, $\sigma_s = 0.0183$ S/m.

271 Complementary electrical characterization of tholins are available in literature (see
272 Table 1). In particular, *Rodriguez et al.* [2003] and *Paillou et al.* [2008] measured the
273 complex permittivity of tholins obtained from a 2% methane atmosphere in the Ku-band
274 (namely at 10 and 13 GHz) and at 77 K to support the analysis of the Cassini Radar ob-
275 servations *Elachi et al.* [2004]. *Paillou et al.* [2008] reported a permittivity of 1.17-j0.0033
276 for a "non-compacted sample" of tholins and of 2.33-j0.0206 for a "compacted sample".
277 These values are logically below the ones measured at lower frequencies as explained in
278 section 3.2. It would have been useful to know the actual porosity of the samples inves-
279 tigated in the Ku-band in order to determine the permittivity of bulk tholins in this fre-
280 quency range as we did in the 1 Hz-100 kHz domain (section 3.1). However, we do know
281 that the "compacted samples" were obtained with a press tonnage of 15 t, which suggests
282 that their porosity is at most 10 % [Paillou, personal communication] hence a maximum
283 permittivity of 2.55-j0.025 based on the Maxwell-Garnett law. Interestingly, we note that
284 the dielectric constant of tholins is larger than that of water ice at low frequencies while it
285 is the opposite in the Ku-band.

286 More recently, *Brouet et al.* [2016] measured the dielectric constant of tholins syn-
287 thesized from a 5% methane atmosphere in the frequency range 50 MHz-2 GHz but at a
288 warm temperature of 243 K.

289 Therefore, contrary to water ice, tholins do not seem to fully lose the frequency
290 dependence of their dielectric constant at very low temperature. The main polarization
291 mechanism responsible for the dielectric constant of water ice is the reorientation of H₂O
292 molecules. This mechanism is greatly affected by temperature and this explains why the
293 dielectric constant of water ice loses its frequency dependence at temperature below about
294 150 K [Mattei et al., 2014]. In the case of tholins, the polarization mechanisms at stake
295 must be more complex and more numerous. Their investigation is out of scope of this pa-
296 per.

297 4 Titan's subsurface composition at the Huygens Landing site

298 4.1 State of art: permittivity of Titan's near-surface, case of the HLS

299 The first estimate of the dielectric constant of Titan's near-surface was derived from
300 observations from the Arecibo radar system: *Campbell et al.* [2003] found a range of di-

301 electric constants of 1.5-2.2 with a mean value of 1.8 for Titan's 26 °S latitude band (we
302 recall that the Huygens landing site is at a latitude of 10.3 °S). After the arrival of the
303 Cassini probe at Saturn, the Radar on board (operating at 13.78 GHz, *Elachi et al.* [2004])
304 provided new and spatially resolved constraints on the dielectric constants of Titan's near-
305 surface both in its real-aperture active (scatterometry) and passive (radiometry) modes.

306 The analysis of the scatterometry data yields dielectric constants in the range 1.9-
307 3.6 with a mean value of 2.2 [*Wye et al.*, 2007]. This analysis is based on raster scanning
308 of large regions at a resolution of about 100 km. No comprehensive investigation of the
309 dielectric constant of the HLS has been published yet. However, it probably exhibits a
310 dielectric constant close to that measured in the plains of Titan, namely, 2.12 ± 0.07 [*Wye*
311 *et al.*, 2007].

312 Radiometry insights into the surface dielectric constant come in two flavors. First,
313 when the spacecraft is far away from Titan (25 000-100 000 km), the disk is scanned
314 twice in two orthogonal polarizations (the spacecraft is rotated between the two scans).
315 These polarization pairs can be used to produce a global map of the surface dielectric
316 constant [*Janssen et al.*, 2009, 2016]. This map is essentially low resolution (300-500 km)
317 except for a few regions that could be observed in mid-resolution in the two orthogonal
318 polarizations during two different flybys. This is fortunately the case of the HLS region
319 for which the dielectric map has a resolution of about 100 km and indicates a value of
320 1.7 ± 0.2 . For comparison, the global dielectric map displays values in the range 1.0 (no
321 polarization plus some allowance for error)-2.25 with an average of 1.54.

322 Second, the radiometry observations collected at all resolutions (from 5 to 500 km)
323 can be used to build a mosaic of Titan's surface emissivity at 2.2-cm at normal incidence
324 [*Janssen et al.*, 2009, 2016]. The emissivity map has a resolution of about 5 km at the
325 Huygens landing site, which has been observed several times at closest approach. It indi-
326 cates an emissivity of 0.94 ± 0.01 , which implies, if this region does not depart too much
327 from a Kirchhoff surface, an effective dielectric constant of 2.7 ± 0.25 .

328 The discrepancy between the effective relative permittivity derived from the polar-
329 ized radiometry measurements (1.7 ± 0.2) and the effective relative permittivity derived
330 from the emissivity at normal incidence (2.7 ± 0.25) suggests that Kirchhoff's approxima-
331 tion does not apply in general to the HLS region. Surface small-scale roughness or, more
332 likely, volume scattering from the subsurface must be invoked in order to reconcile these
333 two observations, although their different resolutions may play a part too. The average ef-
334 fective dielectric constant at 13.78 GHz of the Huygens landing site region must thus lie
335 between 1.5 and 3.0 as also suggested by the scatterometry analysis.

336 The imaginary part of the complex permittivity of Titan's surface was not measured
337 by the Cassini Radar/radiometer but the analysis of the seasonal thermal wave points to a
338 mean 2.2-cm emission depth in the range 40–100 cm for the dominant radar-dark terrains,
339 consistent with the value ϵ_r'' of tholins as measured by *Paillou et al.* [2008][*Janssen et al.*,
340 2016].

341 Lastly, the permittivity probe PWA-MIP/HASI on board the Huygens probe mea-
342 sured both the real and imaginary parts of the complex permittivity of the HLS in the
343 EVL (Extremely and Very Low) frequency range. At 45 Hz (frequency for which the
344 PWA-MIP calibration is best), *Hamelin et al.* [2016] found $\epsilon_r' = 2.55 \pm 0.35$ and ϵ_r'' in
345 the interval 0.2 – 0.8 for the first 11 min after the landing and $\epsilon_r' = 2.35 \pm 0.35$ and ϵ_r'' in
346 the interval 0 – 0.1 after. These values are consistent with the ones previously published
347 [*Grard et al.*, 2006] but with more reliable error bars that account for uncertainties related
348 to the probe's resting attitude on the surface.

349 More importantly, we highlight that the sounding depths of the Cassini Radar/radiometer
350 and of PWA-MIP/HASI are similar: both instruments are sensitive to the composition and
351 structure of, roughly, the first meter below the surface [*Hamelin et al.*, 2016; *Janssen et al.*,

2016]. More specifically, in the case of PWA-MIP/HASI it is a weighted volume average of the first meter with a weight decreasing with depth (for a more in depth discussion see *Lethuillier* [2016]). All the observations mentioned above are reported in Table 2. They are further discussed in the following section.

4.2 Constraints on the composition of the HLS from dielectric measurements

Based on the values presented in Table 2 and assuming that they are all representative of the HLS, we put some constraints on the composition of the subsurface in this region.

The range of permittivity values reported in section 4.1 is consistent with the expected dielectric constants of materials relevant to Titan (see Table 1). More specifically, permittivity values derived from microwave observations overlap those of solid and liquid hydrocarbons. They preclude solid sheets of water ice but not water ice in a porous form. Indeed, we highlight that the values reported above are effective dielectric constants; they depend on both the composition and physical state of the surface/subsurface. In particular, they are affected by the subsurface porosity. As a consequence, microwave observations do not proscribe a fractured, porous water ice surface which would exhibit an effective dielectric constant much smaller than 3.15, the dielectric constant of bulk water ice. Likewise, while low-frequency observations preclude a compacted layer of tholin-like organics they do allow tholins as part of the near-surface composition. Assuming that the composition of the first meter below the surface is a ternary mixture of water ice, tholin dust and pores (empty, partially or fully filled with liquid methane), we use both microwave and PWA-MIP/HASI results to constrain the respective proportion of these ingredients.

For that purpose, we also assume that Titan's tholins are similar to those synthesized in laboratory from a mixture 95/5 of N_2/CH_4 as this is the gas mixture that produces the largest abundance of solid aerosols [*Sciamma-O'Brien et al.*, 2010]. Further, based on the idea that the real part of the permittivity of liquid methane at 94 K should be identical at near-DC and microwave frequencies, we use the same value of 1.67 in both frequency domains as measured by *Leese et al.* [2012] at 100 Hz (see Table 1). Unfortunately, this latter assumption cannot be made for the imaginary part of the permittivity for which no measurement at PWA-MIP/HASI frequencies is available in literature. As a consequence, as long as the low-frequency electrical properties of liquid hydrocarbons are not investigated in laboratory, the PWA-MIP/HASI measurements of ϵ_r'' cannot be used to place constraints on the composition of Titan's near-surface. However, we highlight that the ϵ_r'' value measured by PWA-MIP/HASI just after landing (see Table 2) is larger, by one or even two orders of magnitude than the expected values for tholins and water ice (see Table 1). Since liquid hydrocarbons likely also have a small loss tangent (as measured in laboratory in the microwave domain (see Table 1) and shown to be true at the surface of Titan by *Mastrogiuseppe et al.* [2014]), PWA-MIP/HASI measurements suggest that an extra conductive material is present at the HLS. The removal of this material may explain the sudden drop of conductivity recorded 11 min after the Huygens landing. This hypothesis is further discussed in section 4.3.

Figure A.6 shows the lower and upper limits of the volumetric fractions of the three considered ingredients of the near-surface as derived from the microwave (red) and PWA-MIP/HASI (blue) observations using the Hashin-Shtrikman bounds of the Maxwell-Garnett mixing formula [*Hashin and Shtrikman*, 1962]. These limits are shown on ternary diagrams; where they intercept (gray area) is the most likely composition of the first meter below the surface of the Huygens landing site. This derivation was done assuming that the subsurface pores are saturated by liquid methane (Figure A.6a), filled with 50% of liquid methane (Figure A.6b) and empty (Figure A.6c). Constraints from microwave observations are obtained assuming a dielectric constant of 2.2 ± 0.1 (see section 4.1). Note that our approach requires a good estimate of the dielectric constant of the HLS which is not avail-

403 able to date, especially in the microwave domain. However, our goal here is to show that,
404 if both the microwave and ELF dielectric constants of the ground were known with a good
405 accuracy, we would be able to reliably constrain its composition because the constraints
406 associated with these measurements are “perpendicular” to each other. This method could
407 prove to be very valuable to future surface investigations of Titan.

408 While not very constraining, some lessons can be extracted from these diagrams.
409 In particular, it seems that some porosity (at least 15%) and the presence of the water ice
410 (at least 8%) are absolutely required to explain Cassini-Huygens observations while that
411 of tholins is not. This means that the subsurface of the HLS could, in theory, consist of
412 a porous water ice layer (60-75% water ice and 25-40% porosity if the pores are empty).
413 However, the composition is most likely a combination of water ice and organic dust with
414 some porosity, as suggested by the images taken at the surface by the Huygens probe and
415 most of the plausible combinations displayed on Figure A.6. If the nature of the dust is
416 tholin-like then its volumetric fraction in the first meter below the surface is at most 50-
417 60%. Coherently, when the occupancy rate of the pores by liquid methane increases, less
418 water ice and/or tholins are required in the mixture. The porosity should vary in the range
419 15-40% for empty pores and 30-65% for saturated pores.

420 **4.3 Constraints on the composition of the HLS from the 11-min event**

421 This work also offers the opportunity to investigate further the implications of our
422 favorite scenario for the sudden drop of conductivity (or ϵ_r'') observed by the PWA-MIP/HASI
423 instrument about 11 min after the Huygens landing [*Hamelin et al.*, 2016] (see also Table
424 2).

425 **4.3.1 Description of observations**

426 The conductivity drop observed by PWA-MIP/HASI occurred in a very short amount
427 of time (2-4 s) and concerns an area, below the Huygens lander, as wide as the distance
428 between the MIP electrodes i.e. 1-2 m [*Hamelin et al.*, 2016]. We reiterate that the con-
429 current observed decrease in ϵ_r' is not strong enough (relative to measurement uncertainty)
430 to be considered significant. On the other hand, the HASI temperature sensors on board
431 the Huygens probe did measure a significant drop of 0.2 K at the same time [*Hamelin*
432 *et al.*, 2016] and the Huygens GCMS (Gas Chromatographer Mass Spectrometer) recorded
433 a continuous increase in the atmospheric methane suggesting the progressive vaporization
434 of methane in the subsurface due to heating by the probe [*Lorenz et al.*, 2006; *Niemann*
435 *et al.*, 2010]. Additionally, the formation of a dewdrop was observed in a camera image
436 and could be linked to rising air with high methane humidity also due to the heating of
437 the surface by the bottom of the probe [*Karkoschka and Tomasko*, 2009]. Lastly, an unex-
438 plained attenuation was observed approximately 10 min after landing in the measurements
439 performed by the acoustic instrument located near the bottom of the probe [*Lorenz et al.*,
440 2014].

441 **4.3.2 Favored scenario**

442 Based on these observations and the fact that the initially measured value of ϵ_r''
443 (0.5 ± 0.3) is much higher than the values expected for water ice and tholins (see Table
444 1) we favor the following course of events:

- 445 1. The Huygens probe was internally heated by internal power dissipation by the pri-
446 mary batteries during the descent and on the surface (around 250 W, [*Lorenz*, 2006]).
- 447 2. After landing, part of the heat was dissipated in the atmosphere by convection, the
448 remaining being dissipated in the ground by conduction with the total heat dissi-
449 pated being around 350 W [*Lorenz*, 2006].

- 450 3. This heating leads to the vaporization of a portion of the subsurface liquid hydro-
451 carbons filling the pores.
- 452 4. An outgassing burst occurred about 11 min after landing and removed a thin super-
453 ficial layer of dust responsible for the observed conductivity.

454 The vaporization of liquid hydrocarbons and, above all, the removal of a superficial
455 conductive dust layer would explain the observed drop in the near-surface electrical prop-
456 erties. Such removal would affect mainly the imaginary part of the subsurface permittivity,
457 as observed. We note that the final value measured by PWA-MIP/HASI (ϵ_r'' in the interval
458 0–0.1) is compatible with a subsurface composed of any combination of water ice, tholins
459 and vacuum.

460 As a further argument [Lorenz, 2006] estimates that a total of 500 kJ of energy
461 could have been transferred to the subsurface in about an hour after landing. This would
462 be sufficient to evaporate approximately 1 cm of liquid methane (approximately 0.91 kg).
463 This value reduces to 0.2 kg if we take into account the possibility that the probe bounced
464 before finding its final resting position (as suggested by Schröder *et al.* [2012]) reducing its
465 contact with the surface (we consider a contact area 4 times smaller than Lorenz [2006]).
466 Of importance, the penetrometer on board the Surface Science Package (SSP) of the Huy-
467 gens probe detected the presence of a 7-mm dust layer at the landing site [Atkinson *et al.*,
468 2010]. This layer is likely composed of organic particles of low-density, therefore easily
469 removable by the vaporizing of subsurface liquid.

470 4.3.3 Source of the conductivity

471 In the scenario previously mentioned the source of the conductivity is a thin layer of
472 dust located at the surface and the removal of this layer would cause the observed drop in
473 conductivity. Although solar UV can cause photoelectron production at planetary surfaces,
474 in the case of Titan the UV flux is completely absorbed by the atmosphere and so this ef-
475 fect cannot influence the near-surface environment. Another possibility is the ionization of
476 the near-surface atmosphere by decay of ^{14}C . According to [Lorenz *et al.*, 2002] the decay
477 rate near the surface is capable of producing 10^4cm^{-2} ion pairs leading to a high air con-
478 ductivity possibly detectable by PWA-MIP/Huygens. The outgassing from the subsurface
479 could have led to the removal of the radiocarbons close to the probe therefore reducing the
480 atmospheric conductivity in the vicinity of the instrument. This scenario could be mod-
481 eled in order to evaluate the maximum conductivity of the atmosphere close to the lander
482 and to appraise whether or not the atmospheric conductivity could explain the conductiv-
483 ity measured by PWA-MIP/HASI. However, the accurate modeling of this phenomenon
484 and the addition of a highly conductive atmosphere near the Huygens probe is not a sim-
485 ple task and out of the scope of this work. In addition, we consider this scenario unlikely
486 compared to the one described below.

487 Our favored explanation for the measured conductivity at the HLS after landing is
488 the existence of a superficial layer of dust material with a non negligible intrinsic con-
489 ductivity. In order to constrain the required characteristics, namely the thickness and con-
490 ductivity, of this putative superficial conductive layer, we conducted numerical simula-
491 tions with a finite element code (COMSOL MultiphysicsTM, see [Hamelin *et al.*, 2016] for
492 more detail) assuming a 2-layer subsurface. The numerical simulations take in account the
493 whole of the Huygens probe (for numerical reasons the probe’s shape had to be simplified,
494 see [Hamelin *et al.*, 2016] for the details of the simplification) in its two extreme attitudes
495 at the surface (see [Hamelin *et al.*, 2016] for a description of these extreme cases). Per-
496 forming numerical simulations for a set of thicknesses of the dust layer we provide esti-
497 mates of the dust electrical conductivity required to explain the observed drop in electrical
498 conductivity 11 min after landing. Figure A.7 shows the resulting upper and lower limits
499 of the imaginary part of the effective permittivity of the conductive layer as a function of
500 its thickness (the upper and lower limits include the uncertainty on the probe attitude at

501 the surface, whereas the error bars account for the numerical error of the model and the
502 measurement uncertainty of the PWA-MIP/HASI instrument). We note that if the thick-
503 ness of the removed conductive layer is 7 mm (as suggested by [Atkinson *et al.*, 2010])
504 then the imaginary part of its permittivity must be relatively high, namely between 2.8
505 and 16.0 (corresponding to a conductivity in the range 7-40 nS/m). Logically, the required
506 imaginary part of the permittivity decreases as the thickness of the conductive layer in-
507 creases; its lower limit is 0.5 ± 0.3 .

508 **4.3.4 Composition of the dust layer**

509 Regarding the implications of this investigation on the composition of the putative
510 conductive 7 mm superficial layer, we are unfortunately hampered by the lack of available
511 information in literature on the conductivity of materials relevant to Titan's at low temper-
512 atures and low frequencies. One thing is certain: the tholins studied in this work do not
513 have a high enough imaginary part to be a major component of this layer. Likewise, the
514 DC conductivity of polyacetylene at 200 K is at most 10^{-7} S/m⁻¹ and shows a linear de-
515 crease with temperature [Jones *et al.*, 1991], preventing it from being a major component
516 of this layer. On the other hand, some polymers, such as polyaniline, or in general, nitrile-
517 rich organic compounds may be more conductive but their accurate electrical properties
518 remain unknown [Le Gall *et al.*, 2016]. Also, nanophase iron and nanophase hematite
519 which are present in Saturn's rings and on the surface of Iapetus [Clark *et al.*, 2012] may
520 have relatively high conductivity at low frequencies/low temperatures: Nikolic *et al.* [2012]
521 measured the DC electrical conductivity of hematite doped with Zn and, by extrapolating
522 their results at Titan's surface temperature, the maximum conductivity is found to 10^{-8}
523 S/m, therefore, the possibility that hematite (doped with 10% Zn) as a major component
524 of this layer cannot be excluded but is very low (the highest conductivity value of this
525 component is only slightly higher than the lowest possible conductivity of this layer, addi-
526 tionally, this only applies to hematite with high Zn content, higher than 10%). Although
527 no measurement of electrical properties of nanophase iron relevant to Titan were found
528 in the literature, powdered metals tend to have a high conductivity. Therefore nanophase
529 iron is most likely at least somewhat conductive and could be a potential component of
530 this layer. Lastly, we note that the photochemical aging of Titan's aerosols during their
531 sedimentation through Titan's atmosphere [Couturier-Tamburelli *et al.*, 2018] and possibly
532 also at the surface can produce aerosols that are more conductive than the "fresh" tholins
533 synthesized in laboratory and analyzed in this work. Future works should consider investi-
534 gating the electrical properties of "processed tholins".

535 **5 Conclusion and perspectives**

536 The measurements performed by the PWA-MIP/HASI/Huygens/Cassini-Huygens in-
537 strument in 2005 provided unique insights into the electrical properties of the first meter
538 of Titan's subsurface. However, in order to convert these measurements in term of com-
539 position, the low-frequency and low temperature electrical properties of materials possibly
540 present at the surface of Titan need to be known. In this paper, we present the first low
541 frequency electrical characterization of samples of tholins. Tholins are organic matter,
542 possibly analogous to the aerosols produced in the atmosphere of Titan and then deposited
543 onto the surface. Their electrical characterization was performed with a dedicated mea-
544 surement bench developed at LATMOS. We find that the electrical properties of tholins
545 follow predictable variations (i.e., the real and imaginary parts of the permittivity decrease
546 with higher frequency, higher porosity and lower temperature) and show significant varia-
547 tions as a function of the composition of the gaseous mixture from which they were pro-
548 duced. Based on multi-frequency laboratory electrical characterizations and combining
549 measurements from PWA-MIP/HASI and the Cassini Radar, we derive constraints on the
550 composition of the Huygens Landing Site. While not very strong (a porosity between 15%

551 and 65%, a maximum of 60% of tholins and between 20% and 75% of water ice) our re-
552 sults and approach can serve as a frame of reference for future studies.

553 We also expand the study of the sudden and significant drop of conductivity ob-
554 served about 11 min after the landing of Huygens at the surface of Titan which was pre-
555 sented in *Hamelin et al.* [2016]. Our favored scenario describes how the subsurface was
556 heated by the probe after landing enough for some subsurface methane to vaporize . This
557 vaporizing methane may have then depleted a thin superficial conductive dust layer. Based
558 on this scenario and numerical simulations we estimate the imaginary part of this conduc-
559 tive dust layer to be at least 2.8 which is very high and rules out the tholins we studied
560 as a main component of the putative superficial dust layer. To our knowledge there is no
561 material relevant to Titan’s surface composition with such a high conductivity (more pre-
562 cisely, the only known possibility would be hematite with a high quantity of Zn). How-
563 ever, the electrical properties of a great number of possible materials remain to be investi-
564 gated and we therefore emphasize the need for more laboratory characterization over wide
565 range of frequencies.

566 Lastly, we note that this work and our analysis approach will be useful for future
567 missions to Titan and, in particular, missions including a permittivity probe such as the
568 Dragonfly mission [*Turtle et al.*, 2017], a relocatable quadcopter recently pre-selected for
569 the New Frontiers program. If the mission is selected, Dragonfly permittivity measure-
570 ments will most likely be more accurate than those performed by PWA-MIP/HASI and
571 will therefore provide much stronger constraints on the plausible composition of Titan’s
572 subsurface and even discriminate between the different types of tholins at the surface .
573 We also note for future missions to Titan, that, in order to differentiate between the differ-
574 ent composition of tholins based on their electrical properties, certain frequencies would
575 be more useful than others. More specifically, at Titan’s surface temperature, while the
576 real part shows significant difference between compositions at all frequencies (see Figure
577 5 left), the most relevant frequencies to capture differences in the imaginary part due to
578 composition are 100, 1000 and 5000 Hz (see Figure A.4a.).

579 **A: Measurements and derivation of the sample complex permittivity**

580 The spectrum analyzer measures the complex impedance of the sample between the
581 electrodes sweeping the frequency range 1 Hz-100 kHz. For a given frequency, the same
582 measurement is repeated 3 times and the average value is recorded. It takes about 22 s to
583 measure the complex impedance over a full frequency spectrum. At the end of a typical
584 measurement cycle which lasts about 20 h (10h for the liquid nitrogen to evaporate and
585 10 hours for the sample to return to room temperature), 3000 to 4000 spectra have been
586 collected.

587 The measured complex impedance Z_s (in Ω) is related to the capacitance C (in F)
588 of the parallel plate electrodes by:

$$589 \quad C_s = \frac{1}{2\pi f j Z_s} \quad (\text{A.1})$$

590 where f is the frequency of the input signal.

591 The complex capacitance of a parallel-plate capacitor is itself related to the complex
592 relative permittivity of the medium between the parallel electrodes by:

$$593 \quad \epsilon_r = \frac{C_s d}{A \epsilon_0} \quad (\text{A.2})$$

594 where $A [m^2]$ is the surface area of the electrodes (and generally of the sample) and
595 $d [m]$ is the thickness of the sample.

596 Equation A.2 applies well if the distance between the electrodes remains much smaller
597 than their dimensions. In addition, it assumes that the electrical field is entirely concen-
598 trated in the dielectric medium between the plates and thus neglects edge effects which
599 induce parasitic capacitances.

600 In order to correct measurements performed on samples from parasitic effects, we
601 calibrate them by measurements made with an empty cell i.e., measurements performed
602 after removing the sample from the sample holder but without changing the distance d
603 between the electrodes. More specifically, we measure Z_{void} and thus C_{void} and equation
604 A.2 becomes:

$$605 \quad \epsilon_r = \frac{C_c d}{A \epsilon_0} \quad (A.3)$$

606 with C_c the corrected complex capacitance:

$$607 \quad C_c = C_s + \frac{\epsilon_0 A}{d} - C_{void} \quad (A.4)$$

608 The effects of the electronics were evaluated and found to be negligible.

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Table A.1. Electrical properties of material relevant to Titan’s surface at 94 K and at 2 frequencies, namely that of PWA-MIP/HASI and that of the Cassini Radar.

Frequencies	45 Hz		14 GHz	
	ϵ'_r	$\epsilon''_r \times 10^{-2}$	ϵ'_r	$\epsilon''_r \times 10^{-3}$
Tholins 2%	4.00 ± 0.04	1.05 ± 0.03	1.17 (non-compacted) ^b 2.33 (compacted) ^b	3.3 (non-compacted) ^b 20.6 (compacted) ^b
Tholins 5%	4.40 ± 0.05	1.68 ± 0.13	N/A	N/A
Tholins 8%	3.40 ± 0.04	1.37 ± 0.04	N/A	N/A
Water ice	3.15^a	0.40^a	3.13 ± 0.30^a	1.30 ± 0.26^a
Liquid methane	1.67^d	N/A	1.74 ± 0.03^c	$(4.93 \pm 2.50) \times 10^{-2c}$

^a Extrapolated from *Mattei et al.* [2014], ^b [Paillou et al., 2008]

^c [Mitchell et al., 2015], ^d [Leese et al., 2012] at 100 Hz.

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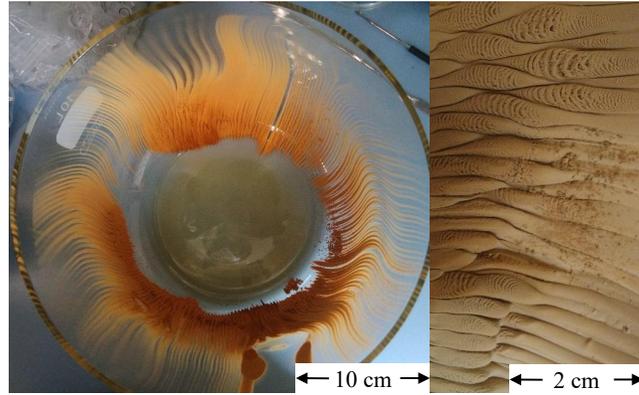
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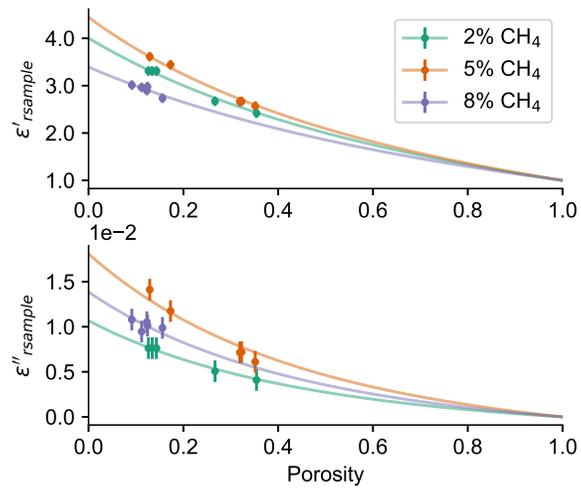
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Figure A.1. Tholins produced by the PAMPRE experiment with a gas mixture of 92/8 ratio of N₂/CH₄.



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Figure A.2. Real (top) and imaginary (bottom) parts of the complex permittivity of tholins as a function of the porosity of the samples measured for three different compositions. The data points are for a temperature of 94 K and a frequency $f = 100$ Hz. The continuous lines represent the Maxwell-Garnett mixing law.

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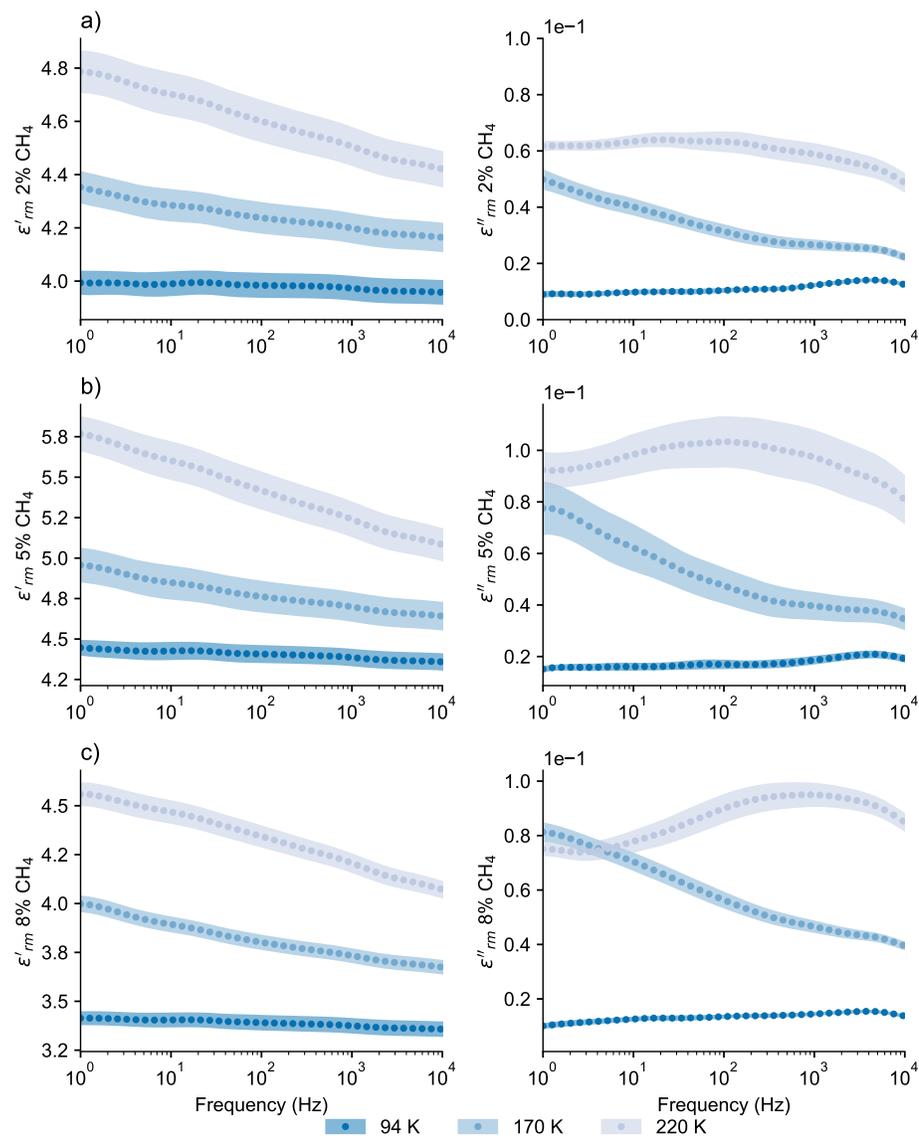
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Table A.2. Remote sensing (from the Earth and the Cassini spacecraft) and in-situ (with the Huygens probe)

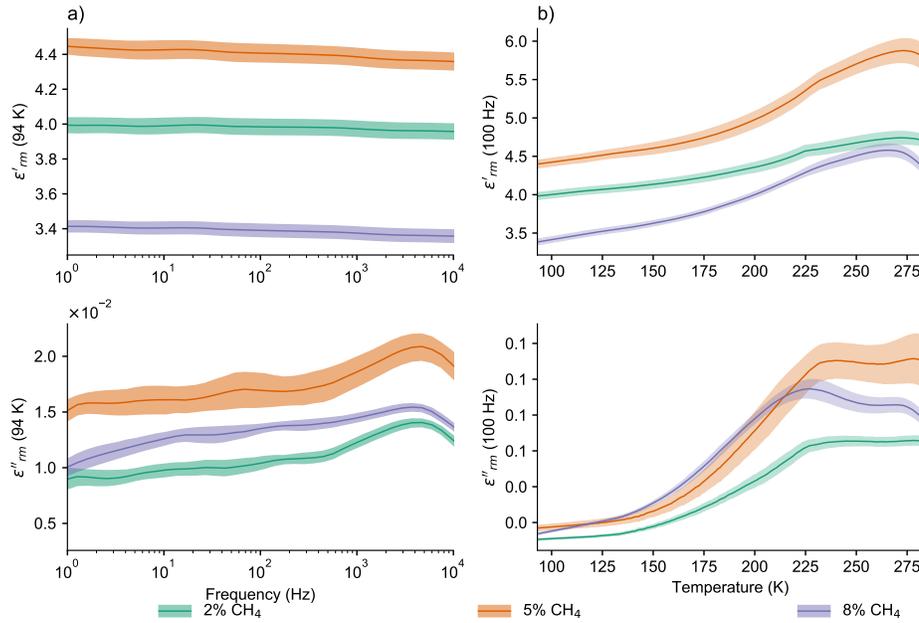
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measurements of the electrical properties of the first meters of Titan's subsurface.

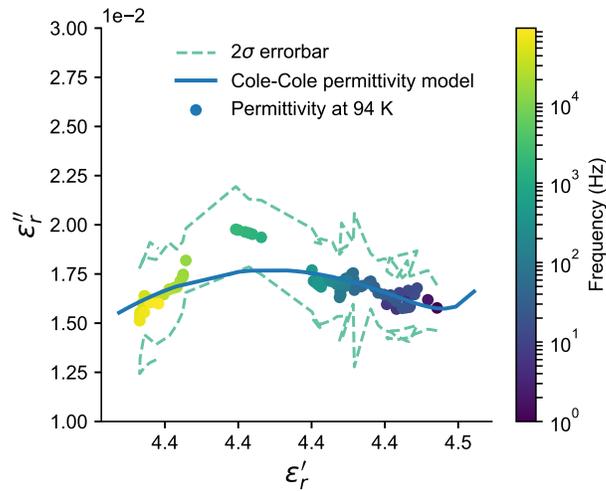
Instrument	Frequency (wavelength)	Region	ϵ'_r	ϵ''_r	Reference
Arecibo Radar System	2.4 GHz (13 cm)	Latitude band at 26°S	1.5-2.2 with a mean value of 1.8 ± 0.3	N/A	[<i>Campbell et al.</i> , 2003]
Cassini Radar Scatterometer	13.8 GHz (2.2 cm)	Average over globe	2.12 ± 0.07	N/A	[<i>Wye et al.</i> , 2007]
		Plains (HLS-like?)	1.9-3.6 with a mean value of 2.2 ± 0.05	N/A	[<i>Wye</i> , 2011]
Cassini Radar Radiometer Polarized	13.8 GHz (2.2 cm)	Average over globe	1.54	N/A	[<i>Janssen et al.</i> , 2016]
		HLS region	1.7 ± 0.2	N/A	
Cassini Radar Radiometer Emissivity	13.8 GHz (2.2 cm)	HLS region	2.7 ± 0.25	$\approx 10^{-3}$	[<i>Janssen et al.</i> , 2016]
PWA-MIP/HASI	45 Hz	HLS	2.55 ± 0.35	0.2 – 0.8	[<i>Hamelin et al.</i> , 2016]
			(<11 min)	(<11 min)	
			2.35 ± 0.35	0 – 0.1	
			(>11 min)	(>11 min)	



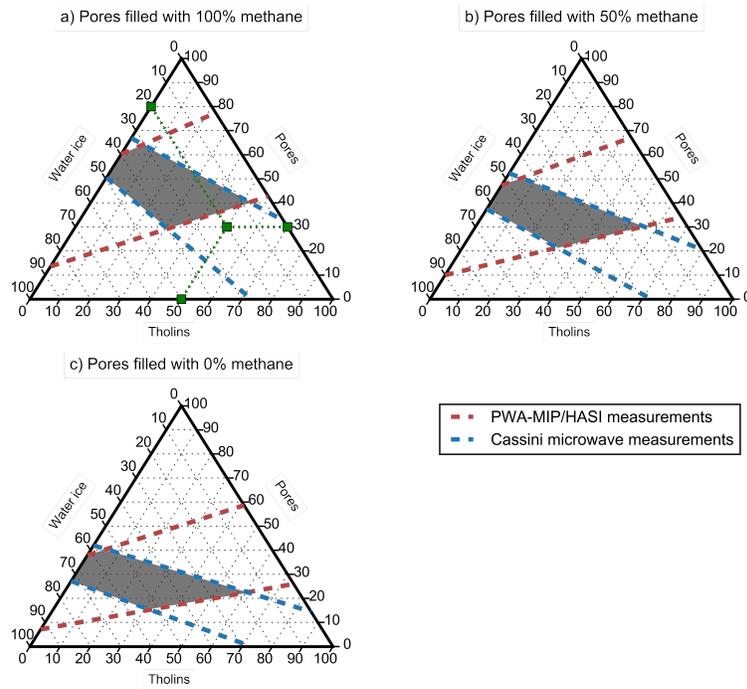
898 **Figure A.3.** Real and imaginary parts of the complex permittivity of bulk tholins as a function of frequency
 899 for three different temperatures and compositions (2% (a), 5% (b) and 8% (c) of methane in the initial gas
 900 mixture).



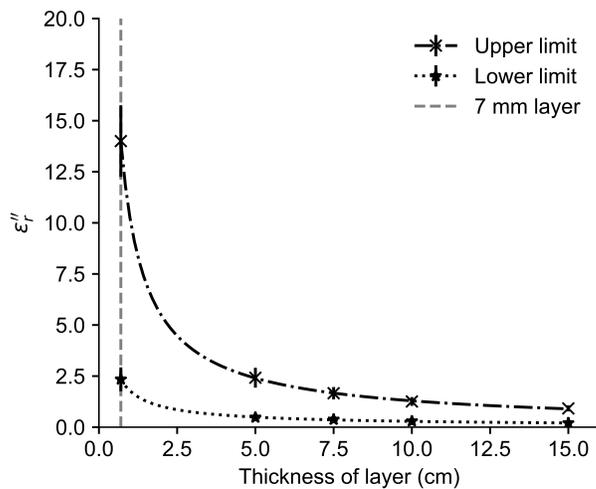
901 **Figure A.4.** Frequency (at a temperature of 94 K, column a) and temperature (at a frequency of 100 Hz,
 902 column b) dependence and of the real and imaginary parts of the complex permittivity of bulk tholins obtained for 3 gas mixture compositions.
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904 **Figure A.5.** Complex permittivity at a temperature of 94 K in the complex plane. The best Cole-Cole fit is
 905 also represented. The scales for ϵ'_r and ϵ''_r are different in order to provide a readable figure.



906 **Figure A.6.** Ternary diagrams showing the constraints on the composition of the Huygens Landing Site
 907 as derived from both PWA-MIP/HASI (red) and the Cassini Radar (blue) observations and assuming that the
 908 subsurface pores are saturated with liquid methane (a), half-filled with liquid (b) or empty (c). The intersec-
 909 tion of the constraints (gray area) represents the most likely composition of the first meter below the surface
 910 of the HLS. To help read this diagram, an example is shown (green squares) on the figure, corresponding to a
 911 mixture of 30% pores, 50% tholins, and 20% water ice.



912 **Figure A.7.** Upper and lower limits of the imaginary part of the permittivity of the superficial conduc-
 913 tive layer required to explain PWA-MIP/HASI measurements. These limits were obtained by using the two
 914 extreme cases of the probe attitude at the surface of Titan. The values at 7 mm were extrapolated