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Research article

The Polyperfluoromethylisopropyl Ether used as a surface tensiometry tool for non-invasive quality assessment of peloids (TVS mud index®): An overview.

Davide Rossi [1,2]

1. Development Cooperation BAZH NGO, Tirana, Albania
2. Association BAZH.I., Maserada Sul Piave, Treviso, Italy

* Correspondence: davide.rossi.bazh@gmail.com

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Abstract: Background Surface tensiometry consented to characterize the surface free energy of geomaterials in an integrated and non-destructive way.

A new surface tensiometry tool, based on the contact angle measurement of Polyperfluoromethylisopropyl Ether (TVS mud index®), has thus developed in the early 2000s. The TVS mud index® was for the first time employed from 2005 to 2010 for surface tensiometry characterization of peloids for pelotherapy from Abano Terme and Montegrotto Terme (Pa-dova, Italy). We aim to report the surface tensiometry application in the thermal field, and show the potentialities of TVS mud index as a marker for the non invasive quality control of the peloids and their maturation process.

Methods The determination of the typical chemical-mineralogical characteristics of a Euganean Thermal Mud (ETM) and their surface tensiometry allowed us to demonstrate the link between the chemical data from X-ray fluorescence (XRF) analysis and they performed using a tensiometer to assess the quality of the peloid and its biological maturation process.

Results The liquid test Polyperfluoromethylisopropyl Ether-based demonstrated the link between variations in volume elements and surface free energy of muddy matrices. The research results here showed that the TVS mud index® is linked to the chemical pattern of peloids.

Conclusions The research work implemented in the period 2005-2010 showed the potentialities of surface tensiometry in the assessment of peloids for pelotherapy using Polyperfluoromethylisopropyl Ether as a liquid test.

Keywords: peloids; surface tensiometry; contact angle; Rossi factor; Polyperfluoromethylisopropyl Ether; Euganean Thermal Mud; X-ray fluorescence

1. Introduction

Peloid, or thermal mud, is a natural complex matrix containing organic and inorganic elements that give it specific functions.

Thermal mud derives from the manual or automatic mixing action in contact with thermal water.

The maturation process of thermal mud is due to the biological action of microalgae that produces organic substances developing in characteristic thermal water. These substances give thermal mud antirheumatic and anti-inflammatory properties [1].

The maturation of thermal mud is performed at 48 °C and is monitorable through the analysis of physical and biochemical changes due to the action of thermophilic microorganisms [2].

The thermal mud components and their variations under the biological maturation process are investigable using destructive and invasive ways such as High-performance liquid chromatography analysis (HPLC), Gas chromatography-mass spectrometry (GC-

MS), and solid phase microextraction (SPME) [1]. From a mineralogical viewpoint, thermal muds and clays, in general, are commonly characterized using X-ray diffraction (XRD), Fourier Transform – Infrared analysis (FT-IR), Scanning Electron Microscopy (SEM), Cation exchange capacity (CEC), Differential Scanning Calorimetry (DSC), and Grain Size Analysis (GSA) [3].

From a surface viewpoint, some research was performed to characterize the influence of sedimentation on the surface tension of bentonites' aqueous slurries to eliminate the influence of sedimentation on the surface tension of dispersed systems [4]. Clayey geomaterials such as peloids can be investigated using surface tensiometry to characterize the surface free energies of many geomaterials in a non-destructive way. Surface tensiometry applied in clay sciences demonstrates that contact angle is related to the surface thermodynamic properties of the solid (s) and liquid (l) via the Young equation for clay minerals [5].

Based on these studies, for the first time, the introduction of surface tensiometry applied to peloids for pelotherapy made it possible to create a polar plot by Excel radar chart of these complex systems. Surface tensiometry allows the projecting and control of natural and formulation systems as they come into contact with the skin and mucous membrane [6-8].

Surface tensiometry can reveal the surface free energy properties of each solid system using the conversion model Owens-Wendt&Rabel-Kaelbe (OWRK) as a reference mathematical model to determine their dispersive (DC: mJ/m2) and polar components (PC: mJ/m2) [9, 10].

Euganean Thermal Muds (ETM) has been characterized in the early 2000th from surface free energy viewpoint [7] employing for the first time the Polyperfluoromethylisopropyl Ether Fomblin HC/25®PFPE (from 2021 PFPE Oil C-250®) as liquid test in the thermal field. The thermal research field is a particular sector that studies the chemical-physical nature of geomaterials for therapeutic use (thermalism). The surface tensiometry application in peloid research opened new perspectives of innovations in the thermal muds research field and peloid quality assessment [7].

PFPE Oil C-250® represents the commercial name of a class of Polyperfluoromethylisopropyl Ether (called perfluoropolyether) that replaced the Fomblin HC/25®PFPE [11-15] (Table 1).

Table 1: Polyperfluoromethylisopropyl Ether nomenclature (Fomblin HC/25®PFPE)

INCI Name	**Polyperfluoromethylisopropyl Ether**
IUPAC Name	Trifluoromethyl-poly[oxy-2-trifluoromethyl-1,1,2-trifluoroethylene]-poly[oxy-difluoro-methylene]-trifluoromethyl ether
Other Chemical Names	Perfluoropolyether (PFPE), Perfluorinated polyether, Polyoxyperfluoroalkane
CAS Name & Number	1-Propene,1,1,2,3,3,3 —hexafluoro-, oxydized and polymerised - 69991-67-9
EINECS Number:	Not applicable (since it is a polymer)
ENCS Name & Number (J)	Perfluoro[copolyalkylene(propylene and methylene)]polyether - (7)-2095
CLS Name & Numbers (J)	Perfluoropolyether

The perfluoropolyether (PFPE) is obtained by oxidative photopolymerization of hexafluoropropene. PFPEs are odorless, colorless, and transparent liquid polymer.

Thanks to the high presence of fluorine (68%), the Perfluoropolyether has the highest electronegativity, low surface tension, low inter-molecular forces, high resistance of carbon-fluorine (C-F) bond, and high stability [11-15].

These characteristics give PFPE hydrophobic, lipophobic, and self-repellent properties together at vapor permeable, insoluble in organic solvents, chemically-biologically inert, and non-flammable properties.

Fomblin HC/25®PFPE (PFPE Oil C-250®) employed in the thermal field in the early 2000s pertains to the unmodified PFPE class of products.

From a chemical viewpoint, the energy of the C-F bond (450 versus 414 KJ/mol of carbon-hydrogen bond) explains fluorinated polymers' thermal, physical, and chemical stability. *The C-F bond allows fluorine high stability, which means it isn't available as molecular fluorine or fluoride radical* [11-15]. The weak forces of intermolecular cohesion, due to the barrier constituted by the atoms of fluorine, determine a high gas permeability of PFPEs due to their unipolar characteristics at gaseous molecules such as nitrogen, oxygen, hydrogen and to their high free volume, united at the low glass transition (Tg) of PFPEs [11-15].

The structure shows the single polymeric units united by bonds of an ethereal type. Those bonds provide a characteristic low surface tension to the molecule that depends on the whole perfluoropolyether structure. The presence of ether bonds and the high content of fluorine (68%) provide the molecule addition features of fluidity and capacity to form films [11-15], giving the physical-chemical characteristics of the main Fomblin HC/25®PFPE (PFPE Oil C-250®) used currently (Table 2).

Table 2 : Physic-chemical properties of PFPE's

PFPE[a] properties	**HC[b]/01**	**HC[b]/02**	**HC[b]/03**	**HC[b]/04**	**HC[b]/25**	**HC[b]/R**
Average molecular weight (D)	650	900	1100	1500	3200	6250
Fluorine (%)	70	70	70	70	70	70
Kinematic viscosity at 20°C (cST)	1.25	3	6.5	35	250	1300
Density (g/ml)	1.76	1.81	1.84	1.87	1.9	1.92
Pour point (°C)	-105	-83	-75	-62	-35	-25
Boiling Point (°C)	140	200	230	-	-	-
Vapor tension (mmHg)	10	10^{-1}	10^{-2}	10^{-3}	10^{-5}	10^{-7}
Surface tension at 20°C (dynes/cm)	17	18	19	21	22	24
Refractive index	1.268	1.278	1.283	1.293	1.299	1.302

[a]Perfluoropolyether [b]health Care

More details on the properties of PFPE have cleared by the 3D approach in the study of the molecular structure from which were determined the geometries of an R—OCF2CF2 perfluoropolyether radical calculated by the methods of B3LYP second-order Moller-Plesset perturbation theory (MP2) [16].

Due to their chemical-biological stability, biocompatibility, and above-mentioned physical-chemical properties, these materials were presented in the cosmetic industry in the 80s as ingredients for emulsion, highly lubricious smooth emollients, moisture barriers, skin conditioners, binder and anti-cracking agent, plasticizer, lubricant, slow release agent, and skin protectant [16].

Because of their low Surface Free Energy (SFE: mN/m) and repulsive characteristics, the PFPE has been presented in the surface tensiometry field as a liquid test to detect sensitively way the chemical-physical variations of the nature of complex matrices. PFPE was also presented as a test liquid for the SFE (mJ/m2) in dendrochronology and food science [17, 18]. The Association Development Cooperation BAZH is a Non-Governmental Organization (NGO) with a scientific unit whose goal is to provide a reference database on different scientific disciplines and submit unpublished data.

The present paper reports a surface tensiometry application in the thermalism field performed from 2005 to 2010 at the University of Padova. Thanks to the particular physicochemical properties of PFPE (SFE=18.1±0.18 mN/m, DC=18.0 mN/m, and PC=0.1 mN/m), the research here reported demonstrated that the contact angles (CAs) of PFPE have linked to the typical chemical component (Al2O3) of an ETM. Static tensiometer measured the CAs of PFPE. X-ray fluorescence instrument determined the amount of Al2O3 (%). Chemical and surface tensiometry data were from a panel test made up of Euganean Thermal Muds (ETM) collected near spa centers in the Euganean Hills thermal area called Euganean Thermal Area (ETA) (Abano and Montegrotto Terme - Padova – Italy).The research here reported has been carried out at the Osservatorio Termale Permanente (OTP) (1996-2014), sited inside the Department of Pharmaceutical and Pharmacological Sciences, University of Padova (Italy), in collaboration with the Department of Geosciences of the same University.

Overall, the main aim of our overview was to evidence the importance of the qualification assessment of thermal products using a fast, easy, and non-invasive analytical technique concerning the traditional ones aforementioned above.

The research here demonstrated the efficaciousness of surface tensiometry in the investigation of peloids' biological maturation process also.

2. Materials and Methods

2.1. Materials

Eighteen specimens of peloids from ETM spas were collected to compose a first-panel test.

Specimens were collected at a depth of 10 cm from the surface of peloids because the thickness major involved in the biological maturation process. Sampling was conducted randomly on ready-to-use mud and carried out in triplicate. Specimens were placed in 100-ml PE-HD containers with double stoppers and stored in controlled conditions (4 °C) before analysis.

2.2. Chemical analyses

The specimens were dried, disrupted, pulverized, and then treated at 860°C for 90′ and at 980°C for 180′. The dried samples were diluted at 1:10 with Li2B4O7 after calculation of the Loss of Ignition (L.O.I.).

The mixture has melted at 1150°C, and FeO concentration according to the method of Pratt and Washington. Chemical analysis of the WDS Philips (now PANalytical) PW2400 X-ray spectrometer (Amsterdam, the Netherlands) was carried out at the Department of Geosciences of the University of Padova [7].

2.3. Surface tensiometry analyses

Surface tensiometry analysis is based on the geometric mean approach developed by Owens&Wendt-Rabel&Kaelbe (OWRK) and was used to determine the SFE of the peloid systems tested based on Young's equation [19, 20] (1).

$$\gamma_{WL} = \gamma_{W} + \gamma_{L} \cos \Theta \qquad (1)$$

Where γ_{WL} is the Interfacial Free Energy (SFE: mN/m) at the s/l interface, γ_{W} is the SFE (mJ/m^2) of solid system, γ_{L} is the surface tension (ST: mN/m) of the liquid test, and θ is the CA measured on the systems surface at equilibrium [19, 20].

The total SFE of a solid, or ST of a liquid, γ, *is divided into a dispersive (* γ^{D} *) and polar (* γ^{P} *) component following the formula* $\gamma = \gamma^{D} + \gamma^{P}$. The IFE can be evaluated by the equation (2).

$$\gamma_{WL} = \gamma_{W} + \gamma_{L} - 2\left(\sqrt{\gamma_{W}^{D}\gamma_{L}^{D}} + \sqrt{\gamma_{W}^{P}\gamma_{L}^{P}}\right) \qquad (2)$$

With dispersive γ_{L}^{D} and polar γ_{L}^{P} components of the liquid and dispersed γ_{W}^{D} and polar γ_{W}^{P} components. Combining Equation 1 with Equation 2, a linear regression function can be provided in Equation 3.

$$(1 + \cos\Theta)\,\gamma_{L} / 2\sqrt{\gamma_{L}^{D}} = \sqrt{\gamma_{W}^{D}} + \sqrt{\gamma_{W}^{P}}\,\sqrt{\gamma_{L}^{P}} / \gamma_{L}^{D} \qquad (3)$$

Where intercept $\sqrt{\gamma_{W}^{D}}$ and slope $\sqrt{\gamma_{W}^{P}}$ are the square roots of the dispersive (DC: mJ/m^2) and polar (PC: mJ/m^2) components, respectively, making it possible to assess the SFE of a solid and statistically test the results [21].

Surface tensiometry measurements were performed on ETMs by static tensiometer (Figure 1), directly on untreated mud matrix by CA method with PFPE, diiodomethane (dim), and glycerine (gly) as reference standard liquids. Figure 2 shows the drop profile of PFPE at the interface with a sample of a peloid.

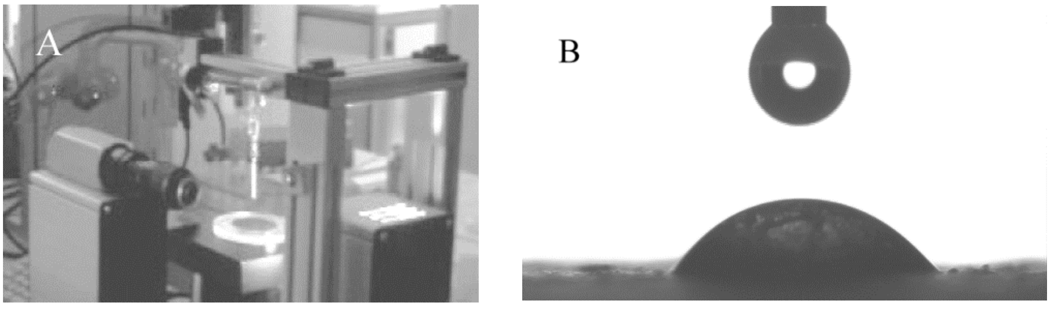

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Figure 1: (A) Tensiometer DSA 10 for Fomblin HC/25®PFPE contact angle measurements and (B) drop profile at Fomblin HC-25/mud interface.

CA measurements were performed on a Tensiometer DSA10-Kruss (Kruss, Hambourg, Germany) combined with specific software directly on the untreated peloid system.

Inserting the values of the CAs and the surface tension components values of the liquid tests in the three equation method of the Owens model, it is possible to determine the SFE of the system and its DC and PC components.

Table 3 lists together the surface tensiometry parameters of the liquid tests (mN/m), their CAs (deg) measured at the surface of the reference thermal mud (Ref. M), and their corresponding SFE profile.

Table 3: PFPE surface tensiometry parameters (Adapted from [3])

Liquids test	CA[a] (deg)	SFE[e] (mJ//m^2)	DC[f] (mJ//m^2)	PC[g] (mJ//m^2)	(1+ cos◎) $\gamma_L / 2\sqrt{\gamma_L^D} = \sqrt{\gamma_W^D} + \sqrt{\gamma_W^P} \sqrt{\gamma_L^P/\gamma_L^D}$
gly[b]	26.1	62.7	21.2	41.5	--------------------------------------
dim[c]	51.2	50.8	50.8	0.0	---------------------------------------
PFPE[d]	59.4	18.1	18.0	0.1	---------------------------------------
				Ref. M	
		56.2	20.3	36.2	

[a]Contact angles, [b]glycerine, [c]diiodomethane, [d]Fomblin HC/25®PFPE, [e]Surface Free Energy, [f]Dispersive Component, [g]Polar Component

Surface tensiometry profiles (SFE, DC, PC) have obtained according to Owens-Wendt (OW) model [6].

2.3.1. *Contact angle measurements at PFPE/peloid interface (Rossi factor)*

The method that led to measuring the CAs at the interface between ETM peloids and PFPE has been developed considering the repellent characteristic of PFPE and surface tensiometry parameters such as drop sharpness (S: px) and snapshot time (t: s). The ratio between S and t is called the Rossi factor (f) (Equation 4) [22].

$$f = S \quad (px)/t \quad (s) \qquad (4)$$

Where f is a dimensionless parameter representing the PFPE CA, S (px), describes the quality of the image-data and is of great importance for the sharpness of the picture taken (snapshot).

Drop age is linked to the snapshot time (t: s) and represents the time elapsed after the first contact between PFPE and peloid. Each PFPE CAs measurement was performed by image snap in the instant in which was detected the best ratio (Rossi factor) between S and t to reach the maximum performance of the repellent characteristics of PFPE at the interface with peloid ($t < 0.5$s).

TVS mud index® polar plot Excel radar chart [6,23] was obtained using an Excel 2000 computer software showing the PFPE CAs measured for each ETM sampled from spas.

3. Results

3.1. Chemical analyses

The levels related to the percentage of Al_2O_3 yielded by X-ray fluorescence (XRF) analysis are in Table 4 [7].

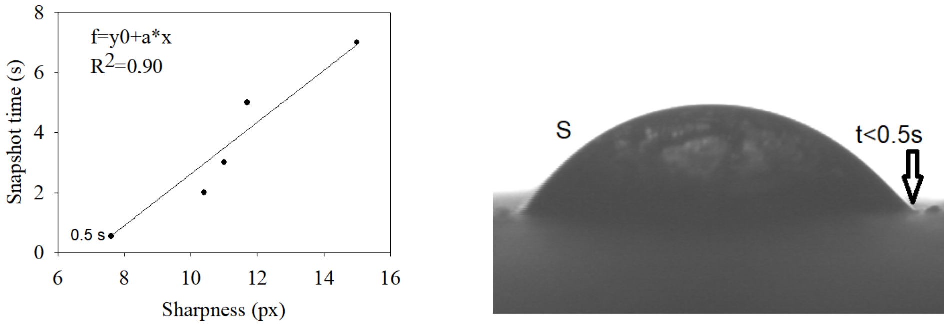
Table 4: Chemical data of Euganean Thermal Mud (ETM) panel test (N=18 and Ref. M) (Adapted from [7]).

%	**SiO_2**	**TiO_2**	**Al_2O_3**	**FeO**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**L.O.I.**	**Tot.**
Ref. M	38.7	0.4	7.7	2.1	0.7	0.2	4.8	17.7	0.9	1.6	0.2	22.3	97.5
1	37.2	0.3	6.6	1.5	1.1	0.1	4.6	20.4	1.1	1.4	0.2	22.6	97.1
2	32.9	0.4	6.8	1.8	1.2	0.1	4.3	23.1	0.9	1.4	0.1	25.1	98.1
3	39.5	0.5	6.9	2.1	1.6	0.1	4.4	17.7	1.0	1.8	0.2	20.5	96.3
4	37.7	0.4	7.0	1.6	1.3	0.1	4.5	20.2	1.1	1.5	0.2	22.5	98.1
5	41.1	0.4	7.2	1.6	1.3	0.1	4.6	17.9	1.2	1.6	0.2	20.8	98.1
6	40.3	0.4	7.3	1.8	1.3	0.1	4.2	19.3	1.1	1.5	0.1	22.0	99.5
7	35.3	0.4	7.3	1.7	1.5	0.1	4.6	21.8	1.0	1.6	0.2	23.9	99.5
8	40.0	0.4	7.6	1.3	1.3	0.1	4.5	19.0	1.3	1.6	0.2	22.1	99.3
9	38.0	0.4	7.7	1.3	1.5	0.2	5.1	18.9	1.1	1.6	0.2	23.8	99.5
10	38.5	0.4	7.7	1.8	3.1	0.1	4.0	19.0	1.1	1.6	0.2	21.4	98.8
11	37.1	0.4	7.8	1.8	1.6	0.1	4.6	19.6	1.0	1.7	0.1	23.9	99.7
12	40.5	0.4	7.9	2.0	1.2	0.1	4.5	17.6	1.1	1.7	0.2	20.5	97.7
13	38.0	0.4	8.1	1.8	1.6	0.1	5.0	18.2	1.1	1.8	0.2	23.6	99.8
14	42.2	0.4	8.2	2.0	1.2	0.1	4.6	17.1	1.2	1.7	0.2	20.9	99.8
15	41.0	0.4	8.4	1.7	1.6	0.1	4.3	16.5	1.1	1.7	0.2	22.6	99.6
16	33.8	0.4	8.6	1.6	3.1	0.1	4.5	21.3	0.9	1.4	0.1	25.2	101.0
17	41.9	0.5	9.4	1.9	1.8	0.1	4.0	16.4	1.1	1.7	0.2	20.4	99.4
18	41.5	0.5	9.6	2.0	2.1	0.1	4.4	16.0	1.1	2.1	0.2	20.4	100.2
19	46.8	0.6	13.4	2.7	2.7	0.1	3.1	10.8	1.1	2.2	0.1	16.5	100.2
Mean	39.1	0.4	8.1	1.8	1.7	0.1	4.4	18.5	1.1	1.7	0.2	22.0	99.0
SD	3.2	0.1	1.5	0.3	0.6	0.0	0.4	2.7	0.1	0.2	0.0	2.1	1.2
CV%	8.3	15.3	18.9	17.5	36.3	15.3	9.4	14.4	8.5	12.8	22.1	9.3	1.2

Table 3 shows the chemical pattern homogeneity of the specimens collected. The calculating L.O.I. led to the evaluation of the weight percentage of elements and compounds removed from the system during the different drying phases. The compounds removed from the system are structural water, CO_2 from carbonatic minerals, organic compounds, SO_2, F, Cl, B, I, and N_2. CaO and MgO (w/w) express the carbonate component, and Al_2O_3 silicate phases are mainly micaceous and clay phyllosilicates [7]. The specimens were successively characterized by XRF/CA combined approach comparing Al_2O_3 concentration with I_{chmi}.

3.2. Surface tensiometry analysis

The degree of correlation between t (s) and S (px) has been assessed after the measurements of PFPE CAs at different time steps. The test has been performed on an ETM sample test (Figure 2).



a

b

Figure 2: (a) Correlation degree between sharpness (S: px) and Snapshot time (t: s) and (b) PFPE drop profile after 0.5s.

The PFPE CAs measurements reached high sensitivity with a t value of <0.5s accordingly with t best compromise with drop sharpness (S: px). PFPE CAs measurements were performed using Rossi factor [22] with a value of 15.2 corresponding to t=0.5s. Figure 3 shows the correlation degrees between PFPE CAs with f and S. In Figure 3 are reported the correlation degrees between PFPE CAs with f and S.

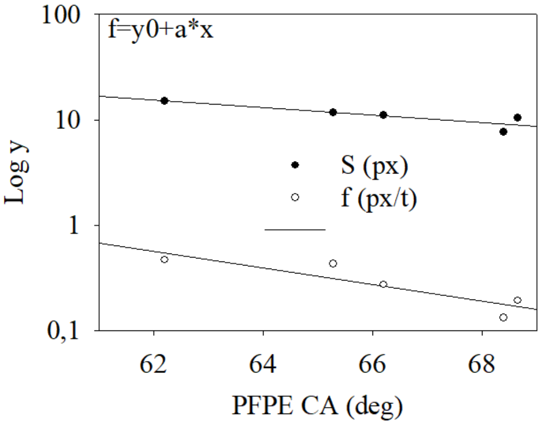


Figure 3: Correlation degrees between PFPE CAs and $\log_{10}$ (S) and $\log_{10}$ (f).

The correlation degree between PFPE CAs and S (R^2=0.83) and f (R^2=0.86) resulted in both satisfactory. The average data related to PFPE CAs (62.2 deg) and f =15 px/s were assumed as reference values because t < 0.5s (t=0.4667s) nearest the most sensitive point at PFPE/ETM sample test (Ref. M) with S (px) value of 7.0005 and constituted the reference value (Ref. PFPE CAs) for all CAs measurements on peloids surface samples collected from ETA.

PFPE was used as a third biocompatible and not mixable liquid to determine the average DC and PC of ETM samples panel test (N=18) to that of Ref. M (SFE=56.1±4.3 mN/m, DC=20.3±1.5 mN/m, PC=35.8±4.8 mN/m) (Figure 4).

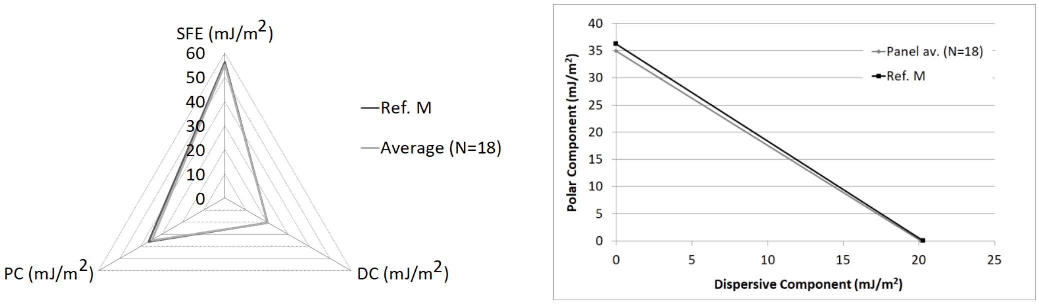


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Figure 4: (a) Polar plot by Excel radar chart reporting the surface tensiometry affinity between Reference thermal mud (Ref. M) [adapted from [7]) and ETMs panel test average (N=18), and (b) Surface Tensiometry Profile.

3.3. XRF/CA combined approach

The SFE data of the panel test, ordered according to Al_2O_3 values, are listed in Table 5 [7].

Table 5: X-ray fluorescence data of Ref. M and panel test (N=18) (% w/w) (Adapted from [7])

	Al_2O_3	**AC[b] (deg)**			**Surface tensiometry parameters (mN/m)**		
		PFPE[c]	**gly[d]**	**dim[e]**	**SFE[f]**	**DC[g]**	**PC[h]**
Ref. M[a]	7.70	59.40±3.68	26.10±2.98	51.00±0.11	56.20	20.30	36.20
1	6.60	61.12±3.73	28.08±3.23	45.86±0.65	55.70	21.20	34.50
2	6.80	54.63±4.08	27.68±2.43	50.30±0.68	62.20	21.20	41.00
3	6.90	57.69±2.22	36.10±1.50	45.80±1.45	51.60	21.70	29.90
4	6.96	57.16±1.92	20.70±0.23	50.30±1.09	58.70	20.80	37.90
5	7.20	64.00±2.55	37.05±2.33	51.70±0.77	50.74	18.84	31.90
6	7.30	64.71±1.44	29.55±3.99	53.05±0.61	54.82	19.11	35.71
7	7.30	55.28±3.21	21.06±2.68	64.27±1.72	58.60	17.80	40.80
8	7.58	57.06±2.54	22.32±3.24	47.40±0.66	58.10	21.40	36.70
9	7.65	62.64±3.22	44.80±1.20	53.30±1.98	46.20	19.40	26.80
10	7.65	55.50±0.45	27.68±3.45	52.01±0.32	55.80	20.70	35.10
11	7.70	56.50±0.64	35.11±2.76	43.01±1.22	52.20	22.40	29.80
12	7.86	64.40±3.76	19.60±3.21	48.50±2.82	59.10	20.10	39.00
13	8.08	53.29±1.76	11.60±3.11	48.15±2.54	61.40	21.80	39.60
14	8.20	62.30±3.41	20.67±2.98	50.60±0.76	58.70	20.00	38.70
15	8.40	58.14±4.12	17.10±2.61	49.06±1.39	59.90	20.90	39.00

16	8.60	60.10±0.43	26.59±1.41	49.60±2.65	56.30	20.50	35.80
17	9.40	55.02±2.22	28.46±3.66	48.90±1.49	55.50	21.40	34.10
18	9.60	73.20±3.82	48.00±2.32	51.50±1.08	43.94	18.17	25.77
19	13.40	84.70±4.00	42.70±4.44	55.80±0.55	47.20	15.60	31.60
Mean	8,06	60.92	27.62	50.48	55.09	20.16	34.93
SD[i]	1,53	7.52	10.95	4.48	5.19	1.67	4.57

[a]reference Mud, [b]Contact Angles, [c]Fomblin HC/25®PFPE, [d]glycerine, [e]diiodomethane, [f]Surface Free Energy, [g]Dispersive Component, [h]Polar Component

The chemical values and PFPE CAs levels were compared to the increase of I_{chmi} levels (Figure 5).

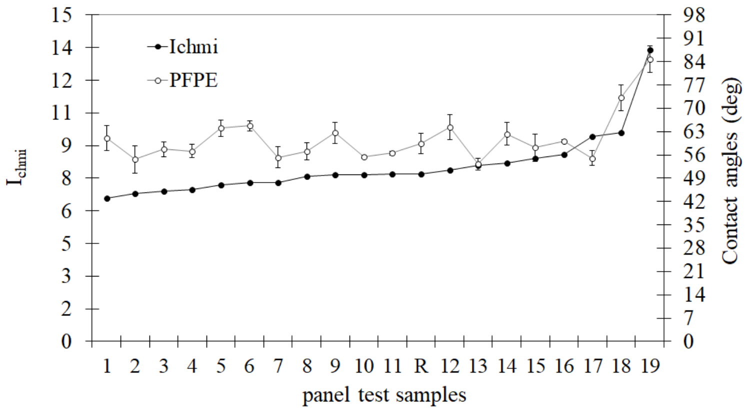


Figure 5: I_{chmi} and PFPE CAs in the ETM panel test (N=18 and Ref. M).

The behavior shown in Figure 5 demonstrated that samples 18 (corresponding to the sample collected numbered 26) and 19 (referring to sample 27) both have high PFPE CAs (73.20±3.82 deg and 84.70±3.43 deg) and I_{chmi} values (9.60 and 13.40).

The links between I_{chmi}, PFPE CAs, and gly were evaluated for samples 26 and 27 as variations in percentage concerning Ref. M CAs levels (Figure 6).

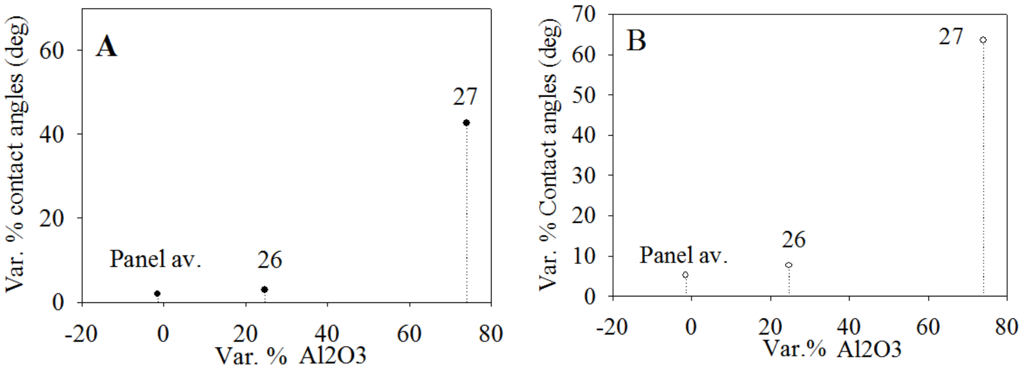


Figure 6: Links between Al_2O_3 percentages and surface tensiometry parameters expressed as variations percentages of PFPE CAs (a) and Glycerine (b) respect to Ref. M CAs.

Figures 6 demonstrated that PFPE CAs variations depend on the polarity changes in the ETMs due to the high presence of water-wetted clay in samples 26 and 27. The extent of the percentage variations of PFPE and gly CAs with respect Ref. M CAs appeared directly proportional to their Ichmi [3]. Figure 7 shows the link between PFPE CA levels and I_{chmi} data [7].

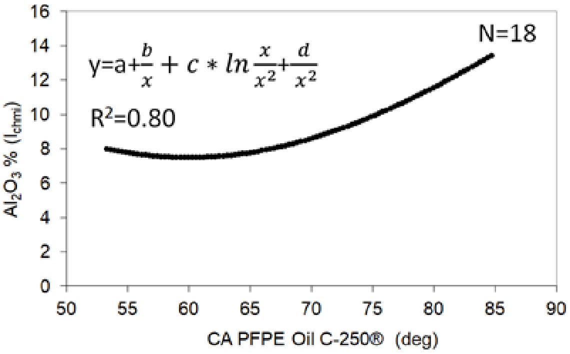


Figure 7: Degree of correlation between PFPE CA and I_{chmi} (Al_2O_3 percentage) (adapted from [7])

Figure 7 demonstrated that the PFPE CAs are particularly sensitive in the presence of the compound more representative of an ETM (Al_2O_3). The chemical-surface tensiometry correlation analysis of ETM samples was satisfactory (R^2=0.80).

Based on these data, correlation analysis has been performed between DC and PFPE CAs measured on the panel test's ETMs (Figure 8).

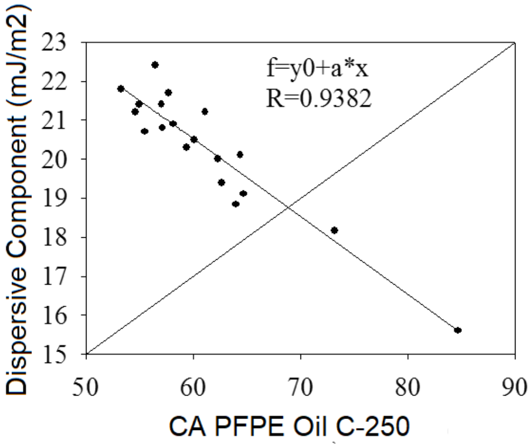
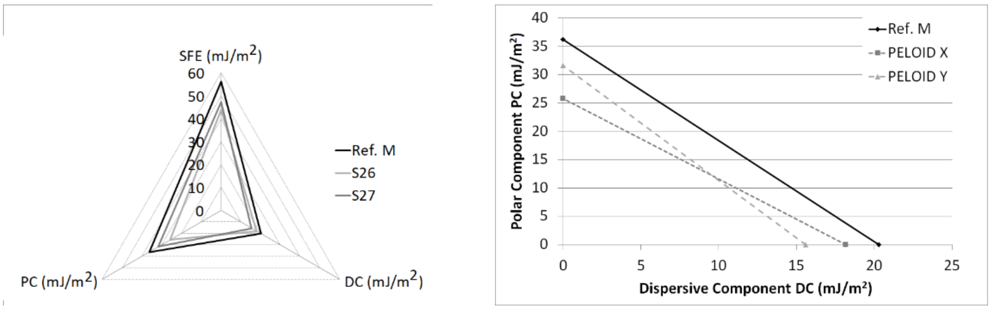


Figure 8: Correlation degree between PFPE CAs and DC of ETMs Panel Test (N=18 and Ref. M)

The results shown in Figure 8 demonstrated the satisfactory correlation degree (R^2=0.94) between PFPE CAs and ETMs DC (N=19). Low PFPE CAs correspond to high levels of ETMs DC, while high values of PFPE CAs link with the high presence of clays in peloids. On the other side, low values of PFPE CAs correspond at ETMs with natural patterns in clay (~2%) that led to a better performance in the maturation process over time.

The presence of higher percentages of clay in peloids (>2%) causes high values in PFPE CAs because of their hydrophilic nature (Figure 9a and 9b).



a

b

Figure 9: (a) Polar plot by Excel radar chart reporting the decrease of DC in peloids with high presence of clay after 45 days of maturation process (adapted from [7]), and (b) Surface Tensiometry Profile.

Figure 9 shows the low presence of DCs in peloids ready for pelotherapy in the presence of increased concentrations of clays concerning Ref. M.

Figure 10 shows the polar plot Excel radar chart of PFPE CAs measured on the ETMs panel test (N=18 and Ref. M) ready for pelotherapy and collected from maturation plants sited N=18 ETA spas after their maturation process.

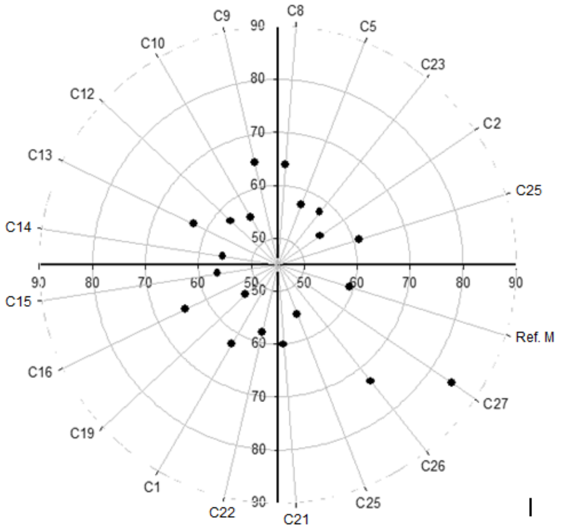


Figure 10: Polar plot Excel radar chart of PFPE CAs measured on ETMs panel test

The polar plot Excel radar chart of PFPE CAs shown in Figure 10 was called TVS mud index® [23, 24]. TVS mud index® values were in accord with the particular properties of PFPE that appeared very sensitive to the variations in I_{chmi} and in the polarity of ETMs. The range of acceptability of TVS mud index® (55.65 deg) was determined according to the average PFPE CAs of N=12 samples of typical ETMs (Ref. M) collected from ETA, which average values corresponded at 59.4 ± 6.2 deg [6].

The determination of the acceptability range allowed the evaluation of the quality of ETMs according to their typical Thermal Area, detecting the variations of their components during the maturation process. Following Figure 5, Figure 10 shows that collected samples numbered C26 (18) and C27 (19) have TVS mud index® levels out of the acceptability range concerning Ref. M because the clayey component was not aligned with their typical pattern.

Figure 11, reports the large-scale TVS mud index® polar plot Excel radar chart of ETMs (N=83) collected after their maturation process and before their use in pelotherapy.

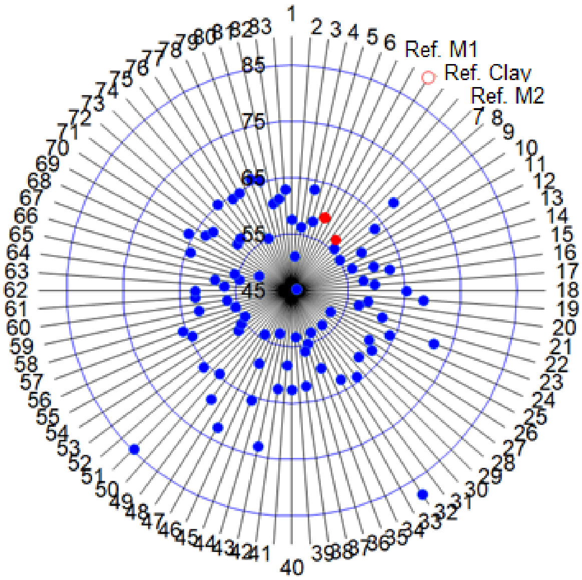


Figure 11: TVS mud index® of I° seasonal monitoring activity (2005/06)

In Figure 11 it is possible to observe a small dispersion rate of PFPE CAs concerning Ref. M (59.4 ± 6.2 mN/m). Figure 12 shows the link between the PFPE CAs and the DC of ETMs involved in that monitoring activity.

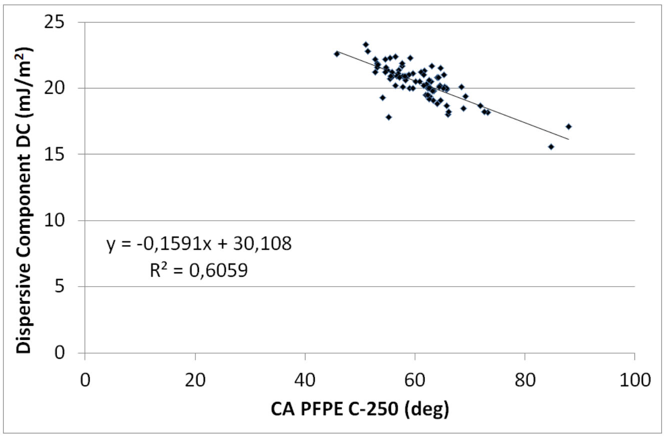


Figure 12: Correlation trend between PFPE CAs and DC of ETMs collected during the I° seasonal monitoring activity (2005/06)

Following Figure 8, Figure 12 confirmed the proportionally inverse between PFPE CAs and DC of ETMs and consequently its link at the maturation process. Figure 13 reports the large-scale TVS mud index® polar plot Excel radar chart of ETMs (N=83 and Ref. Clay, Ref. M 1 and Ref. M 2) collected during an II° seasonal monitoring activity (2006/07).

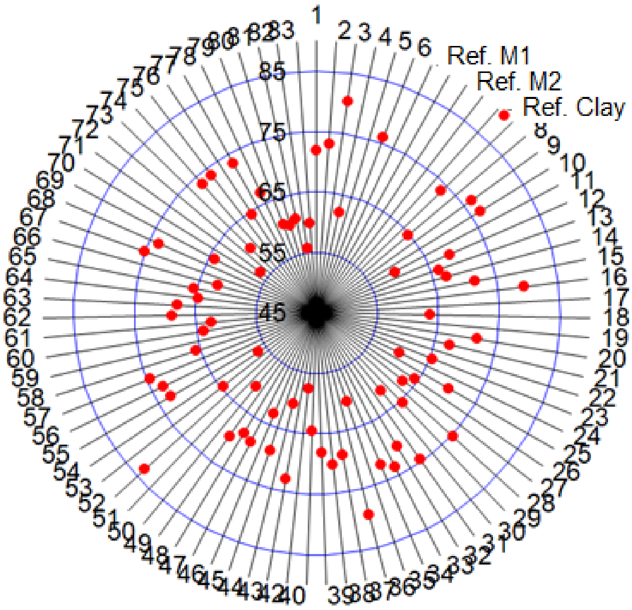


Figure 13: TVS mud index® of II° seasonal monitoring activity (2006/07)

Figure 14 reports the link between the PFPE CAs and the DC of ETMs after the II° seasonal monitoring activity (2006/07).

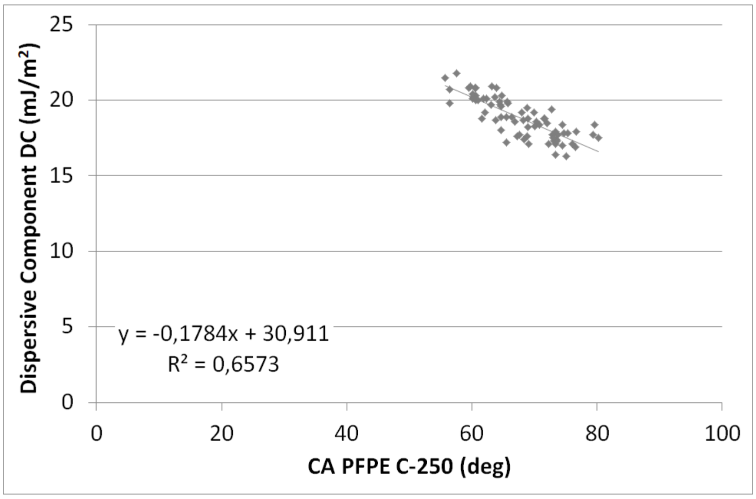


Figure 14: Correlation trend between PFPE CAs and DC of ETMs collected during the II° seasonal monitoring activity (2006/07)

Comparing Figures 11 and 12 with Figures 13 and 14, authors observed a general increase of the PFPE CAs in the II° seasonal monitoring activity (2006/07).

4. Discussion

The research reported here under light that the compounds of ETMs are of pharmaceutical interest owing to their surface tension, interfacial tension, and surface free energy.

From a chemical viewpoint, Al_2O_3 was thus assumed to be an evaluation parameter for typical ETM (I_{chmi} index). The work reported here shows that the variability of PFPE CAs is due to its particularly low SFE (18.1±0.18 mN/m) and polarity null (PC = 0.1 mN/m). Consequently, the PFPE CAs variations seemed to depend strongly on the balance between hydrophilicity and lipophilicity of peloid systems that influence the PFPE/ETM interface about the hydrophobic and lipo-phobic properties of the PFPE.

Ultimately, the difference between I° (R^2=0.6) and II° s(R^2=0,66) seasonal monitoring activities appeared due to a change in the clayey pattern of ETMs and, or a different performance in the maturation processes.

On this basis, the reported experimental observations opened the employability of PFPE, such as hydrophobic, lipophobic, and self-repellent integrated surface tensiometry liquid test for ETM peloids quality assessment.

The experimental evidence observed in the period 2005-2010 was based on the non-invasive and rapid approach to the characterization of peloids complex systems, introducing the PFPE as a surface tensiometry tool for the integrated assessment of the quality of ETM, capable of expressing the variations of their main chemical-mineralogical components such as Al2O3 and its maturation state.

6. Conclusions

The data here reported are related to the research held from 2005 to 2010 and demonstrate that TVS mud index® turns out to be a sensitive parameter for evaluating ETMs in process-dependent conditions, revealing the link between the surface free energy properties and the clayey fraction of ETMs expressed in terms of Al2O3 percentage. The PFPE demonstrated its capability to identify and discriminate ETMs ready to use in pelotherapy about the changes in their components. PFPE, therefore, was assumed as the first surface tensiometry parameter to evaluate the quality of a peloid and the management of their maturation process in maturation plants.

The studies performed in 2005-2010, reported by our Association BAZH NGO, were also conducted for the qualification of artificial Japanese Biofango® and its maturation process performance [19]. The studies performed in ETA (2005-2010) and on Japanese Biofango® (2010-11) opened the possibility of evaluating the potentialities of PFPE in the quality assessment of peloids and their maturation processes.

In our opinion, this novel approach developed in the early 2000s and applied in ETA should revived, critically reviewed in some graphical forms, and optimized, encouraging research institutions to continue the application of surface tensiometry in the thermal field within the multidisciplinary Integrated Analytical Approach (IAA) [25, 26].

More recent surface tensiometry methods using PFPE for liquids characterization [27] could open new perspectives on the non-invasive and rapid quality assessment of spring waters for balneotherapy applications and their effects on the skin surface.

In the end, the studies reported evidence of the importance of the surface tensiometry approach to detect the variations of one or more components in a peloid intended as a complex system.

The surface tensiometry approach performed using the PFPE as a liquid test opens the hypothesis to consider it a non-invasive "quality marker" for peloid characterization because its CA values are very sensitive to the variations of all its organic and inorganic components.

The peloid quality marker appears coherent within the general concept of marker in science by which it has been define as "something that serves to identify, predict, or characterize: such as a distinctive biological or biologically derived indicator (such as a metabolite) of a process, event, or condition (such as aging, disease, or oil formation) [28]. However, the marker concept has been applied in biology, and the definition of a peloid is "mud prepared and used for therapeutic purposes" [28].

On that base, we hypothesized a definition of a marker in thermalism: "something that serves to identify and characterize in a non-invasive way the quality of a mud prepared for therapeutic purposes and its typical biological maturation process under natural and artificial conditions".

7. Patents

Skindecoder®, TVS mud index®, Tenskinmeter®, and Biofango® patents are reported in this manuscript.

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Institutional Review Board Statement: The study reported here was approved by the BAZH NGO Board

Informed Consent Statement: Not applicable because manuscript reported preview research.

Data Availability Statement: Data results said here are from unpublished data; figures and tables were adapted from references where needed. No statistics were reported such from other publications in accordance with MDPI Research Data Policies.

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Conflicts of Interest: The author declares no conflict of interest

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