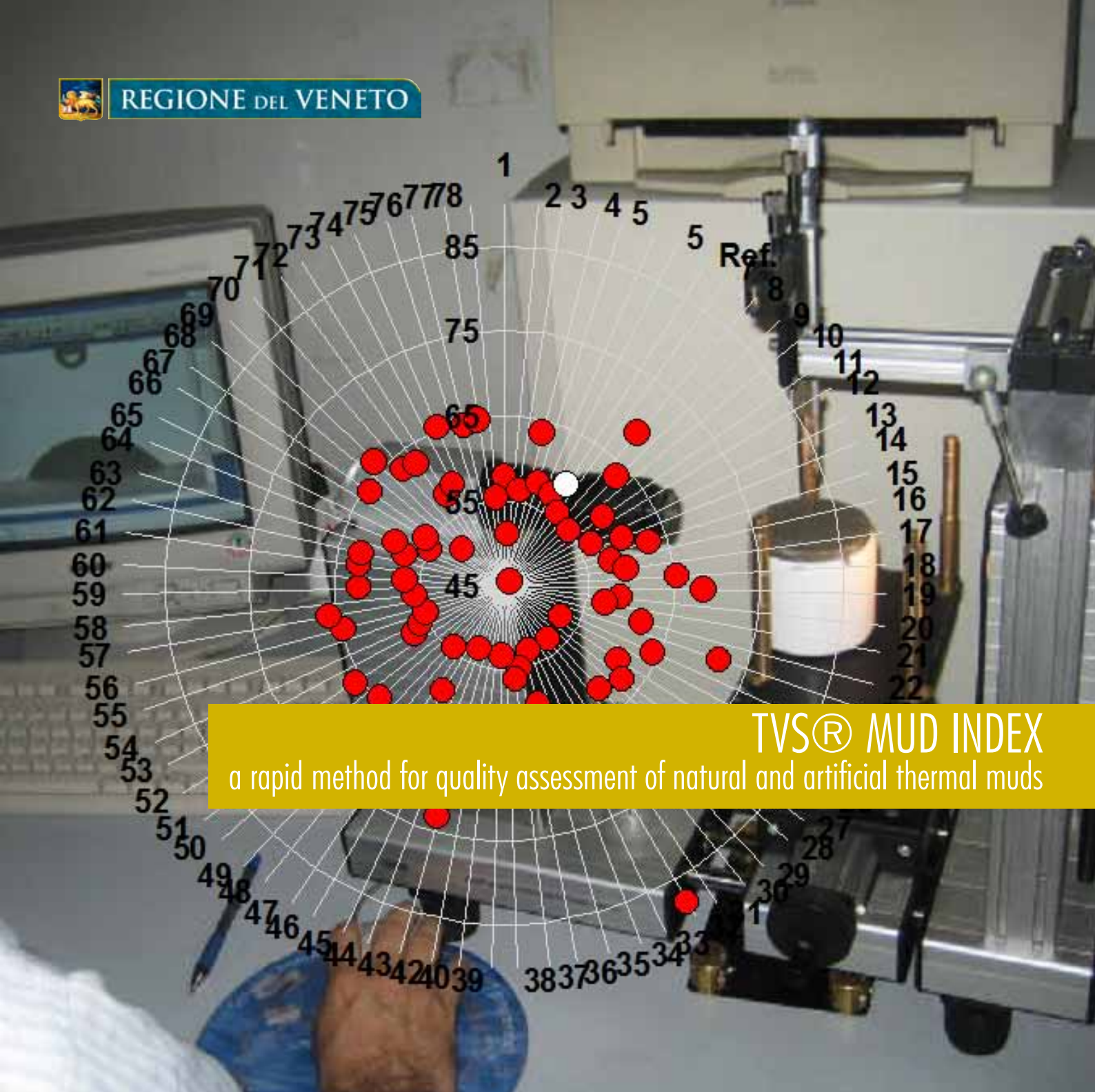




REGIONE DEL VENETO



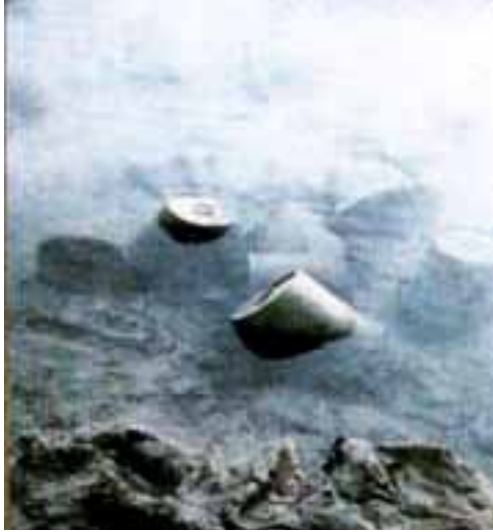
TVS® MUD INDEX

a rapid method for quality assessment of natural and artificial thermal muds

# IDEASS

Veneto, Italy

Innovation for Development and South-South Cooperation



# Introduction

by **Daide Rossi**

TVS mud index® is a simple and fast method to evaluate the characteristics of natural and artificial thermal muds and, consequently, their quality in function of the variations of their composition in the maturation process.

TVS mud index® demonstrated to be so sensitive to different muds, that it can be defined as a real “thermal marker”. It is a physical detector used in thermalism research field which reveals the physical interactions with different components of thermal muds, making them visible and consenting to indicate possible chemical-mineralogical modifications.

Thermal mud is a typical hydrothermal resource product currently employed by many centers in the world for the treatment of the most common inflammatory diseases. The economic impact of pelo-therapy can be considered as an important contribute for the development of the health & wellness tourism sector in countries with significant hydrothermal resources in their territory.

In many countries, pelo-therapy is not well exploited, or it has been developed traditionally, but without scientific criteria. In particular, these countries present a great dispersion of their hydrothermal resources due to low research and development investments, despite of their thermal richness. The development of simple and rapid methods to measure the characteristic of thermal muds, with the collaboration of local institutions as Universities and Research centers, can be a great opportunity for these countries.

TVS mud index® was experimentally developed for the first time in 2005 by the Technical Director of the Permanent Thermal Observatory – OTP, an academic derived structure headed and created in 1996 by the Scientific Responsible Prof. Antonio Bettero of Department of Pharmaceutical and Pharmacological Sciences of University of Padova, promoted by the Veneto Region and working in close collaboration with the University of Padua.

The innovative method was first used in 2005 for characterization of the Euganean Thermal Muds (in Abano Terme and Montegrotto Terme, Italy) and for the determination of their quality during monitoring activity (2005-2009) thanking at the collaboration with the Centro Studi Termali “Pietro D’Abano” (Abano Terme – Padova- Italy). In 2006 it was also tested on BrentaKer® silt, a particular geo-material produced by EGAP company (Rosà - Vicenza, Italy), from the Italian geologic zone called Piana Alluvionale del Brenta constituted by fine silt, a quarry by-product of the mining process. In 2010, the method was used on the Japanese artificial thermal mud Biofango, ideated and developed by Ascendant Inc.(Tokio, Japan) in collaboration with Marukoshi Co., Ltd. (Ishizaki Nanao-city, Ishikawa, Japan) and Sanraku-En Inc. (Tonami, Toyama, Japan), demonstrating to be capable to qualify them on the base of their compositions. TVS mud index® consented to identify a good range of acceptability where each value is associated to a typical thermal mud having specific mineralogical and physic-chemical characteristics compatible with the thermal area where they have been collected. These thermal muds are thus employable in pelo-therapy as they respect their original nature. The identification of this good acceptability range allows to focus the attention only to thermal muds having TVS mud index® values falling out, and consequently saving on the number



Hydrothermal resources in the world

of chemical and mineralogical analyzes, especially in case of long monitoring activities on large populations of samples.

On the basis of these experimental evidences, this innovative method allows evaluating the quality of many kinds of natural and artificial thermal muds as it is interconnected with their typical characteristics and maturation process. Moreover, because of its simplicity, speed and efficiency, it is also strategic for projects aimed to the development of the thermal unused potentials, for the benefit of the economies of the territories. These projects should involve multiple stakeholders (national and local governments, economic actors, local associations) and, for the use of TVS mud index®, universities and research centers in the countries concerned.

The Permanent Thermal Observatory intends to promote internationally this innovative methodology, to improve territorial development and for the benefit of local people.

# What problem does it solve

One of the main problems to face during the development of quality protocols of matrices as thermal muds is the presence of too many components that vary in the time and that should be controlled. TVS mud index® has been developed to study these numerous components in an integrated way.

In the case of the Italian Euganean Thermal Area, the geo-materials are constituted by typical mineralogical components, hot spring water and substances with therapeutic properties derived from the biological activity of a typical Euganean algal flora developed in hot spring water. The contact between

these components produces changes in the time, in the characteristics of the muddy matrix. These changes are linked with the production of many substances where molecules with therapeutic properties are also present. The modification in the time is called "maturation process". TVS mud index® demonstrated to be very sensitive to the variations of the composition and consented to evaluate in fast way the quality of the maturation process steps (only 5-10 minutes for analyses of each sample), demonstrating its suitability for topical application during pelo-therapy.

The identification of a typical acceptability range of natural thermal muds allows controlling the characteristics of the samples collected in each monitored thermal spa, and their maturation process. This method helps to avoid too many chemical analysis for those mud samples that demonstrates good levels of TVS mud index®, directly linked to the characteristics of the thermal collection area, focusing the attention only to samples outside this range.

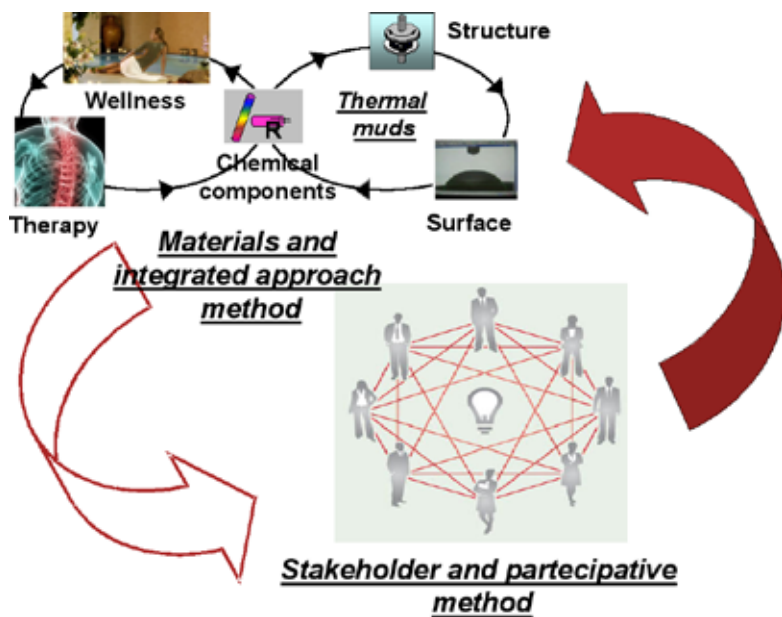
This method helps to solve the problem of the excessive costs of a high number of chemical and mineralogical analyses, saving time in monitoring activity. For example, thermal muds with TVS mud index® levels outside the acceptability range do not represent their geologic zone of collection and consequently they are not conform to their typical specificity. For this reason, TVS mud index® demonstrated particular relevance with refer to the increase of importance of rapid and non invasive qualification of artificial and natural products for human use and, in particular, for therapeutic aims.

The positive supplementary experiences with other kinds of geo materials as BrentaKer® silt, and the Japanese Biofango, confirmed the capability of TVS mud index® to measure in a sensitive and non invasive way the variations of the characteristics of these muddy matrices in the time. In this way the method allows to assess these matrices on the basis of the variations of their components during the maturation processes and, consequently, to know in which moment they present the best therapeutic properties. In particular, studies on Biofango helped to introduce in Japan the concept of pelo-therapy.





## TVS mud index®<sup>®</sup>, in practice



TVS mud index® is a mean for the control of quality and maturation process of geo-materials for human use. It provides a single value, expressed as contact angle, which represents all the components of a general material and is strongly linked to its structure. This methodology is called “integrated approach” at the study of a material.

The aim of this approach is to deepen the knowledge of the links between all the parts of thermal muds, represented by chemical components, structure, surface and to study them simultaneously in function of the time and of their therapeutic properties.

The following items summarize the structural aspects of the use of TVS mud index® for the realization of projects for the development of the thermal potential. For specific technical aspects of innovation, see the bibliography presented in the relevant section of this brochure.

### Technical and scientific management

Based on the experience made by the Permanent Thermal Observatory of Padua, the first step is to create technical and scientific units that can make use of this innovative methodology.

These units could be created in university laboratories or public research institutes interested. Given the relatively technological simplicity and thanks to the low requirements in terms of space, equipment and reagents of tensiometric units, it is not necessary to resort to high level development centers or to previous high technical knowledge. Physicist and chemist with multidisciplinary approach could represent the better reference points to form the equipe.

In the experience of the Permanent Thermal Observatory, the research of new tensiometric methods for the characterization of thermal muds and other geo-materials for topical applications and their quality control by TVS mud index® was held in collaboration with the Department of Pharmaceutical Sciences of University of Padua. With refer to the applications in the field of geo-materials and biomaterials in general, PTO has established collaborations in the University of Padua with the Department of Geosciences for chemical and mineralogical analyses and the Microanalyses Laboratory of the Department of Pharmaceutical Sciences for chemical analyses.

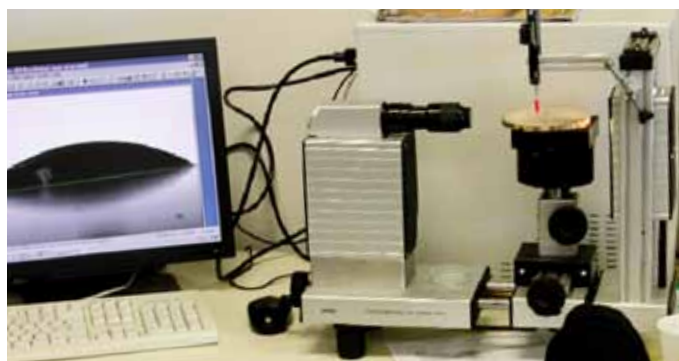
The technicians who will use the methodology of TVS mud index® have been trained through specific training modules. The method of measurement of natural thermal muds surface energy is rapid and easy, and often used by students in Academic Thesis. The duration of training vary in consideration of the needs. For academic aims the duration is approximately one year, as this method is included in a multidisciplinary formative research activity, while for expert researchers the duration can be one month only.



## Equipment

The instrument employed for contact angle measurements is a tensiometer DSA 10 (Germany), which can be easily used and is transportable.

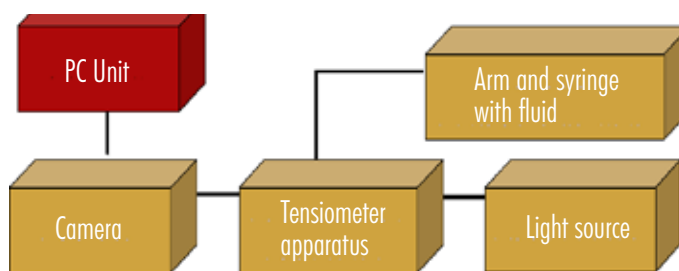
Tensiometer uses small amount of fluid for each contact angle measurement, employing simple accessories fully available in commerce and low cost materials, with easy management and maintenance.



DSA 10 tensiometric unit

## Methodology

The variations of the characteristics of each thermal mud sample influence the variations of the contact angles of Fomblin HC-25 fluid indexed as points in the diagram. The contact angle is expressed in degrees and it forms when a drop of Fomblin HC-25 fluid comes in contact with the surface of a thermal mud. The contact angle can be easily measured by goniometric method.

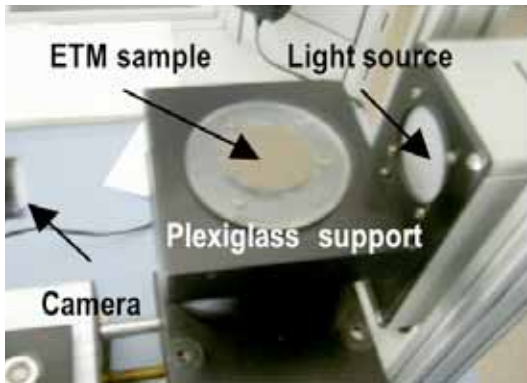


Box scheme of a tensiometer

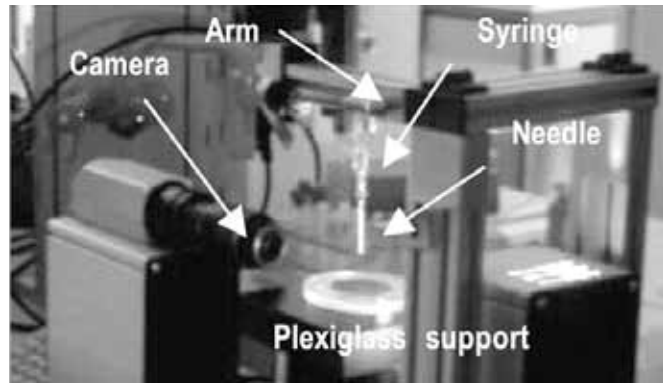
The steps for the measurement of the contact angles of a drop of Fomblin HC-25 on the surface of a thermal mud are very easy and simple. First, the sample preparation of is fast. The picture shows a natural ETM (Euganean Thermal Mud) sample on plexiglas support ready for contact angle analyses. In particular, the picture evidences the position of the needles inserted on syringes containing drops of fluid and mounted vertically over support samples on the arm of the DSA 10 tensiometer, the light source and the camera apparatus to capture the drop image.

A drop of fluid is produced pushing the top of the syringe installed in the arm of tensiometer until it falls on the sample surface. The contact angles formed at the interface with the sample of ETM are measured.

Applying this method on large scale on natural thermal muds to be used in pelo-therapy, is possible to distinguish in a fast and not invasive way the muddy matrices samples, their different composition on the basis of the different contact angles measured. Each point of the TVS mud index® corresponds to a contact angle average value (10 contact angles measurements on the surface of each sample analysed) of drops measured on each muddy surface, related specifically to muds ready to be applied in therapy and collected from each thermal plant.



Plexiglass support with thermal mud (ETM)

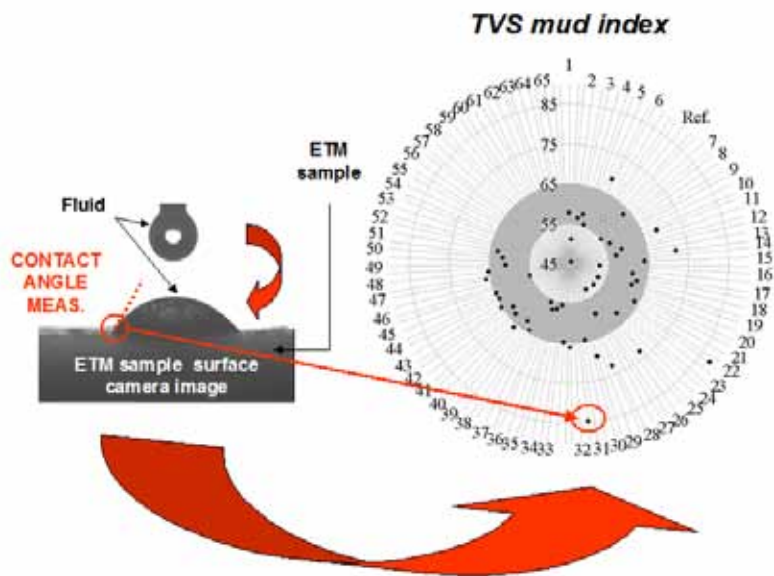


DSA 10 tensiometric unit

The contact angle values of fluid that fall outside the acceptability range of TVS mud index®, demonstrate that those samples are not yet conform to the typical composition of ETM reference and consequently not suitable for pelo-therapy.

The figure evidences: a drop of Fomblin HC-25 fluid in contact with muddy surface; the contact angle formed on the muddy surface that determines the values of TVS mud index® reported in excel graphic and corresponding at each sample.

On the other hand, the maturation process of a thermal mud has particular importance for its therapeutic properties because it is during this process that muds are enriched of substances.



TVS mud index® has demonstrated also its capability to follow the variations in the time of the characteristics of muds during the maturation process, where the variations of the contact angles are linked to the biologic production of many substances with therapeutic properties. This biologic activity modifies the general characteristics of the mud. The easy and fast way in which TVS mud index® levels can be determined could contribute to solve many issues linked to thermal muds monitoring activity for quality assessment of geo materials for topical applications.

# Results

TVS mud index® for quality determination of natural thermal muds can be considered an useful contribute for national and international institutions interested in the development of qualification protocols for typical natural hydrothermal resources of their territories aiming to improve local health&wellness thermal tourism linked to territorial marketing.

According with territorial needs and potentialities, the Veneto Region promoted the Permanent Thermal Observatory (PTO) as a scientific direction of a monitoring network, involving all the interested actors, to determine the maturation process and the quality of natural thermal muds.

In this context, the Permanent Thermal Observatory determined the TVS mud index® of natural thermal mud sample collected in maturation plants of thermal centers during two monitoring cycles, in 2005 and 2006. TVS mud index® was tested on 83 samples ready to be used in pelo-therapy and demonstrated to be an useful mean to detect the variations of the characteristics of natural thermal muds in function of the quality of management of the maturation process plants of each centre.

This consented to evaluate the behavior of the maturation process through the analyses of the variations in the time of the TVS mud index® values of one kind of thermal mud. Considering the variations of the characteristics of muds in the time linked to the decrease of TVS mud index®, it has been possible to assess the maturation process of natural thermal muds, silt and artificial mixtures like Biofango.

In Italy, the TVS mud index® is been widely utilized in prestigious thermal centers as Abano Terme, Montegrotto Terme, Galzignano Terme, and Battaglia Terme (Veneto Region) interested in the qualification process of thermal muds for health purposes. The Italian Ministry of Health is involved in a re-organization process of the entire sector, aiming to acquire more knowledge about the technical preparations of thermal muds and their qualitative monitoring in the time, and some Italian Regions are in contact with PTO to know more about the TVS mud index® with the objective to open at the possibility to start a scientific collaboration.



Compared to other analytical techniques, TVS mud index® allows to obtain a lot of data with a very simple, economic and easy to use apparatus composed only by a light source and a camera positioned in front of it.

In short, considering the tensiometric measurement time distributed in two days (6 hours per day), the time required to process the data and formulate a detailed report also considering that some analyses could be repeated, the total duration of the monitoring activity may be approximately 4-5 days for a single cycle of 80 samples.



Impianto automatico

The economic advantage of this method is based not only on the short time needed for each sample analysis, but also on cost saving due to the very small quantitative of reagents employed. Furthermore, compared to the traditional analytical approaches, this method allow to have physical information directly on the material without subjecting it to physical or chemical pre-treatments

On the basis of these considerations, it could be possible to reduce the costs of a great number of analysis normally needed for the control of many kind of product processes, involving materials in general. In thermal field, this opens new perspectives for the quality control and monitoring of many kinds of geo materials.



Impianto manuale

The TVS mud index<sup>®</sup> method of contact angles measurement (PCAM method) can be also applied to vegetal biomaterials as wood and raw coffee beans. The Département des Sciences Fondamentales of Quebec University (Chicoutimi, Canada) used the method for assessment of surface energy of wood and for statistical analyses. The Caffè del Santo company (Limena, Italy) used the method to study surface energy of raw coffee beans, aiming at improving the research on coffee industrial process showing great interest to continue the collaboration with PTO. Many research proposals was prepared in 2012 in the field of biomaterials also and actually under evaluation.





# International interest

The countries that used these methodologies to qualify muddy matrices from a tensiometric point of view have been Italy (2005-2010) and Japan (2010-11). Italy and Japan are countries with some of the best hydrothermal resources in the world.

The presence of hydrothermal resources, united to public and private institutions sensitive to innovations, are important elements to introduce in the interested countries these multidisciplinary methodologies.

TVS mud index could interest international research public institutions competent in the study of hydrothermal resources, with particular attention to the therapeutic aspects of pelo-therapy, linked to thermal mud maturation process and to the clinical effects of the thermal protocols currently in use.

Moreover, public institutions can involve the private sector in order to define and implement specific projects for territorial market development, through the identification a typical muddy matrix, and focused to eco sustainable thermal tourism. Essential condition for the development of these kind of innovative projects is the participation of universities, research centers, local and central authorities, private enterprises operating in the territory as thermal spas, and organizations as local NGOs.



TVS mud index measurement method was presented by the Technical Direction of PTO at the 1st Congreso Iberoamericano de Peloides (Spain, November 2007), one of the more important international scientific event in the field of pelo-therapy, raising great interest among the participants.

PTO also presented by the author its innovative methodologies in: Brasil (O Fango Termale, Salvador de Bahia, November 2006); Bulgaria (The Permanent Thermal Observatory, Sofia, February 2008); Canada (The TVS Modelling: from the experience of thermal muds to other biomaterials as wood, UQAC University Chicoutimi, September 2009); Albania (The role of the Permanent Ther-

mal Observatory in the field of Hydrothermal resources in Italy and some perspectives in the study of Hydrothermal resources in Albania, Department of Pharmaceutical Sciences Tirana University, November 2010, Faculty of Natural Sciences Tirana University Albania, February 2011); Japan (Economic and health care issues in Eta Spas Activity: the role of Permanent Thermal Observatory in Euganean thermal muds assessment" Morino Uta spa Jozankei Hokkaido, December 2010, Wakura spa Ishigawa, December 2010, Sanraku-en Tonami, December 2010, Toho University Tokio, December 2010, Japan Advanced Institute of Science and Technology JAIST Ishigawa, December 2010.



In Albania, during 2010 and 2011, through a series of PTO missions carried out with the support of the NGO BAZH of Tirana, an international scientific project entitled "Support the developing hydrothermal resources in Albania" has been designed, in close collaboration with institutional stakeholders as the Albanian Academy of Science, the University and the Polytechnic of Tirana. In March 2012, a first formative module on complex matrices with particular attention at TVS mud index use has been realized in collaboration with the University of Tirana under the coordination of the Albanian NGO BAZH.

The simplicity of the method allows to implement other PTO academic observatories in the interested countries, building an international network for quality assessment and process control of local hydrothermal resources which underwent monitoring activity. The Permanent Thermal Observatory of Padua, with its wide experience, can offer scientific and technical assistance to this network. PTO and the University of Padua can provide instruments as tensiometers, know-how, formative modules, and technical-scientific support in the field of geo materials for human use, together with fully availability to host technicians for research stages.



## To know more

For not expert, a specific and well explained video that help to understand the scientific environment in which this method was developed within the PTO scientific activity and the instrumental analyses steps for determine of TVS mud index:

<http://www.centrostuditermali.com/public/Aree/Video/ITA.php?FILE=BetteroITA.flv&W=408&H=328>

The websites of some spas in Abano Terme and Montegrotto Terme can also be visited, where the role of OTP in thermal muds monitoring by TVS mud index is underlined. Keywords for website searching are: "hotel-abano-montegrotto-OTP".

Directed to experts of the sector, here follow a more exhaustive and in-depth documentation on PTO research profile, PTO Technical Director Research activity. Moreover, research papers on TVS mud index are available on-line and at PTO.

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- D. Rossi & A. Bettero (2006), TVS mud index ® 2006C000447
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- D. Rossi, S. Rossi, H. Morin, A. Bettero: Within-tree variations in the surface free energy of wood assessed by contact angle analysis. *Wood Sci Technol* (2012) 46: 287-298 DOI 10.1007/s00226-011-0407-1
- D. Rossi, E. Mioni, M. Zancato, A. Bettero, S. Rossi: Development of a tensiometric model for surface energy characterization of raw coffee beans. *Journal of Food Engineering* (2012) DOI 10.1016/j.jfoodeng.2012.04.006

# Contacts

The Permanent Thermal Observatory is available to provide technical support and innovation transfer to the interested countries. In order to establish collaborations, contact:

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REGIONAL COUNCIL OF VENETO. General Secretariat of Planning - International Relations Directorate  
"Work realized with regional contribution under Regional Law n. 55/1999, Article 5, D.G.R. n. 608 of 09.03.2010".

## Innovation for Development and South-South Cooperation

**The IDEASS Programme** - Innovation for Development and South-South Cooperation - grew out of the major world summits in the 1990s and the Millennium General Assembly and it gives priority to cooperation between protagonists in the South, with the support of the industrialised countries.

**The aim of IDEASS** is to strengthen the effectiveness of local development processes through the increased use of innovations for human development. By means of south-south cooperation projects, it acts as a catalyst for the spread of social, economic and technological innovations that favour economic and social development at the local level. The innovations promoted may be products, technologies, or social, economic or cultural practices.