STATISTICAL ANALYSIS OF XPS DATA FOR WETTABILITY ESTIMATION OF RESERVOIR ROCKS

Yani Carolina Araujo and Mariela Araujo
Exploration and Production Division, PDVSA Intevep. Caracas, Venezuela.

ABSTRACT

The knowledge of the wetting condition of reservoir rocks is relevant for the design of many reservoir exploitation plans in the oil industry. The term wettability describes the affinity of the mineral surface for a particular fluid occupying the pore space of the reservoir rock, when several immiscible fluids are present. Traditional methods for the evaluation of wettability, based on volumetric properties such as displacement tests, are very time consuming, fact that has motivated the search for new approaches to estimate this property.

X-ray photoelectron spectroscopy (XPS) is being used as a faster way to infer the wetting condition of reservoir rocks. XPS allows knowing the detailed chemical composition of the outer layers of a solid surface. In the technique the sample is exposed to irradiation with a soft x-ray source under vacuum, and the energy of the emitted photoelectrons is analyzed. The scattered electrons have an energy characteristic of the element from which they were emitted, and the intensity of the characteristics peaks observed in the energy spectra is related to the concentration of the elements present in the surface.

A statistical analysis of the XPS spectra performed on 132 reservoir rocks is presented here. The analysis is done on the quality of the spectra as well as on the information derived from it, from which wettability ranges are defined in terms of the amount of organic carbon present on the surface. Confidence limits for property values, with accuracy above 91 % are defined to validate each prediction. Most samples used in the study were submitted to imbibition and/or Amott-tests to define their wetting condition and also to validate the information inferred from the XPS data. The preliminary statistical analysis suggests that XPS data can be used to predict the wetting condition of a reservoir rock with a quantified uncertainty.

INTRODUCTION

The term wettability describes the affinity of the mineral surface for a particular fluid occupying the pore space of the reservoir rock, when several immiscible fluids are present. In the oil industry, the wettability condition of reservoir rocks is a key parameter in oil recovery by waterflooding and in well stimulation operations. The wettability of a rock sample strongly affects the waterflooding behavior and flow properties such as the relative permeability because wettability is a major factor controlling the location, flow

and distribution of fluids in porous media. There are several procedures for rock wettability assessment [1], however these are laborious and primarily qualitative.

Previous works have suggested that X-ray photoelectron spectroscopy (XPS) can be used to determine the wettability of reservoir material [2-4]. The XPS technique has been used to elucidate the structural and chemical information of many different types of surfaces. This technique, being sensitive only to the superficial layers of solids, can be used to study surface processes that occurs in the outermost atomic layers of the solid material, therefore can be related to properties such as wettability.

In the XPS technique the sample is exposed to electromagnetic irradiation with a soft x-ray source under ultrahigh vacuum. This radiation is absorbed by electrons with binding energy below the vacuum level, which are then liberated from the solid with a kinetic energy that is analyzed. The scattered electrons have an energy characteristic of the element from which they were emitted, and the intensity of the characteristics peaks observed in the energy spectra is related to the concentration of the elements present in the surface through relative sensitivity factors proper of each instrument. Since electrons with energies as high as 100 eV originate from depths of less than 50 Å, a considerable part of the detected photoelectrons is due to excitations of surface atoms, so the technique can be readily used to evaluate the chemical composition of the outermost surface by identifying the core level energies. The lateral resolution of XPS is 5 mm and its sampling depth is in the order of 20 atomic layers. The technique is non-destructive.

For many freshly exposed fractured surfaces of natural sandstones we examined the relationship between wettability, as measured with the Amott-Harvey test, and surface composition as determined from XPS. Wettability measurements by the Amott-Harvey method give a guide to the relative oil or brine wetting tendency of reservoir rocks. This can be crucial in the selection of relative permeability test methods to generate data relevant to the reservoir situation. The Amott method involves four basic measurements associated to spontaneous and forced displacements, which are described in the experimental section.

The XPS spectra of oil-wet surfaces reveal the existence of organic carbon (C-H) and a silicon specie, of the kind Si-CH found in silane compounds [2], having a well-defined binding energy which differs from that of the Si-O species of the sandstone grains. There exists quantitative evidence [2-4] that chemisorbed organic material on the pore surface defines the oil-wetting character of various reservoir sandstones. The established ranges for XPS wettability are:

- If the C-H content $\geq$ 50%, the sample is oil wet (OW)
- For 49% $\geq$ C-H content $\geq$ 37%, the sample is weakly oil wet (WOW)
- For 36% $\geq$ C-H content $\geq$ 25%, the sample is intermediate wet (I)
- For 24% $\geq$ C-H content $\geq$ 19%, the sample is weakly water wet (WWW)
- And for C-H content $\leq$ 18%, the sample is strongly water wet (WW)

It is interesting to note that the XPS analysis does not allow to distinguish between the intermediate wet and the neutral wetting condition.

In this work we evaluated the accuracy of the XPS technique for wettability analysis. We performed a statistical analysis of the XPS spectra and Amott-Harvey results of 132 reservoir rocks. The analysis is done on the quality of the spectra as well as on the information derived from it, from which wettability ranges are defined in terms of the amount of organic carbon present on the surface. Confidence limits for property values, with accuracy up to 95 %, are defined to validate each prediction This preliminary statistical analysis suggests that XPS data can be used to predict the wetting condition of a reservoir rock with a quantified low uncertainty.

EXPERIMENTAL PROCEDURE

Samples

For Amott-Harvey Wettability Tests

The core samples used in this study were sandstones obtained from different wells of Venezuelan reservoirs. These samples were nominally 2.3 cm in diameter and 4.3 cm in length. Samples were cleaned before the wettability test using the traditional Soxhlet extraction with toluene and methanol.

For XPS Measurements

A rock cylinder of 1 cm in diameter and 3 cm in length was cored under fresh water from each of the core samples. At least two freshly exposed fractured surfaces (1 x 1 x 0.3 cm) were obtained by cleaving from each cylinder. Extreme care was taken to avoid contamination from handling. The surfaces were used immediately to prevent adsorption of air-borne organic species. Sample handling was performed by standard ASTM norms [5].

Fluids

Test liquids for Amott-Harvey wettability tests were mineral oil (Soltrol, $\rho = 0.7794$ g/cc, $\mu = 2.27$ cps) and synthesized formation water (brine) similar to that of the Venezuelan reservoirs.

Amott-Harvey Wettability Test

The core samples were saturated with formation water and then prepared for the Amott-Harvey test by centrifuging under mineral oil until the irreducible water saturation was reached. The Amott-Harvey test of a given sample consisted in four steps: (a) immersing

the sample in water and measuring the volume of oil, V_{osp}, spontaneously displaced by imbibition of water; (b) centrifuging the sample in water until the residual oil saturation is attained and measuring the volume of oil displaced, V_{od}; (c) immersing the sample in oil and measuring the volume of water, V_{wsp}, spontaneously displaced by imbibition of oil; (d) centrifuging the sample in oil until the irreducible water saturation is attained and measuring the amount of water displaced, V_{wd}. The results of the test are expressed by three indices. A water-wetting index, δ_w; an oil-wetting index, δ_o; and a neutral wetting index, δ_n, defined by

$$\delta_w = \frac{V_{osp}}{V_{osp} + V_{od}}, \quad \delta_o = \frac{V_{wsp}}{V_{wsp} + V_{wd}}, \quad \delta_n = 1 - \delta_w - \delta_o. \tag{1}$$

A triangular representation of the three indices allowed discrimination between neutral, intermediate, and fractional wettability syndromes [3,5] (see Figure 1).
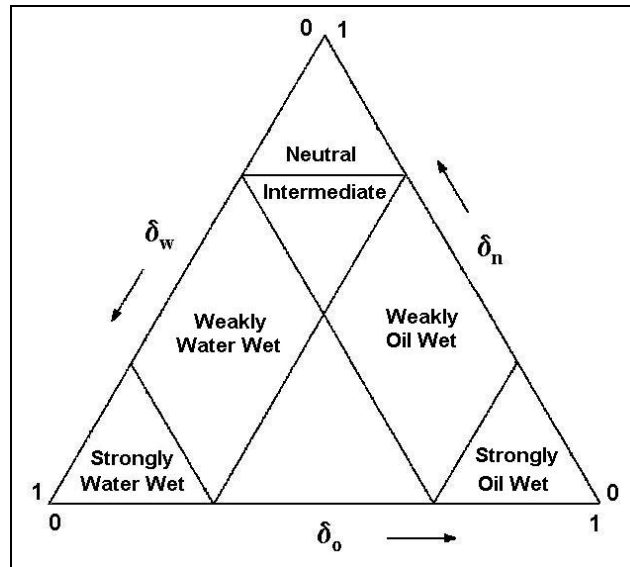
Figure 1. Triangular representation for the Amott-Harvey wettability index.

XPS Measurements

The XPS data were obtained with a Leybold-Hereaus equipment with a LH-11 energy analyzer using a source (380 W) of either Al (13 kV, 30 mA) or Mg (13 kV, 20 mA) Kα X-rays for sample excitation. The base pressure was below 10^{-8} mbar. Data collection was accomplished with a microprocessor interfaced to a PC computer. The SPECS GmbH software "Spectra 5" was used for processing the XPS data. Atomic surface compositions were determined by using the relative sensitivity factors of León and Carraza [6]. Low-resolution survey spectra were first acquired to identify different surface elements. The concentration of each element was then calculated from the area of

the corresponding peak in a high-resolution spectrum; this is the area of a Gaussian line fitted to the high-resolution peak after linear subtraction of background noise.

Statistical Analysis of the XPS Spectrum

A statistical analysis of the XPS spectra was performed on 132 reservoir rocks. The analysis was done on the quality of the spectra as well as on the information derived from it, from which wettability ranges are defined in terms of the amount of organic carbon present on the surface. Confidence limits for property values, with accuracy up to 95 %, are defined to validate each prediction.

RESULTS AND DISCUSSION

The XPS survey spectra of a rock sample reveal the presence of oxygen (1s, 532.2 eV), two forms of carbon: carbon singly bonded to an oxygen atom (1s, 286.5 eV, and carbon singly bonded to a hydrogen atom as in aliphatic chains (1s, 284.6 eV); two forms of silicon: silicon singly bonded to an oxygen atom (2p, 103.5 eV) and silicon bonded to a C-H chain (2p, 102.5 eV); aluminum (2p, 74.5 eV). Some samples also exhibit chlorine (2p, 198.5 eV), magnesium (1s, 1303.5 eV) and sodium (1s, 1071.5 eV) among other elements. The reference line for all the XPS spectra was organic carbon (1s, 284.6 eV). A typical survey spectrum is shown in Figure 2. Adventitious carbon content is negligible.
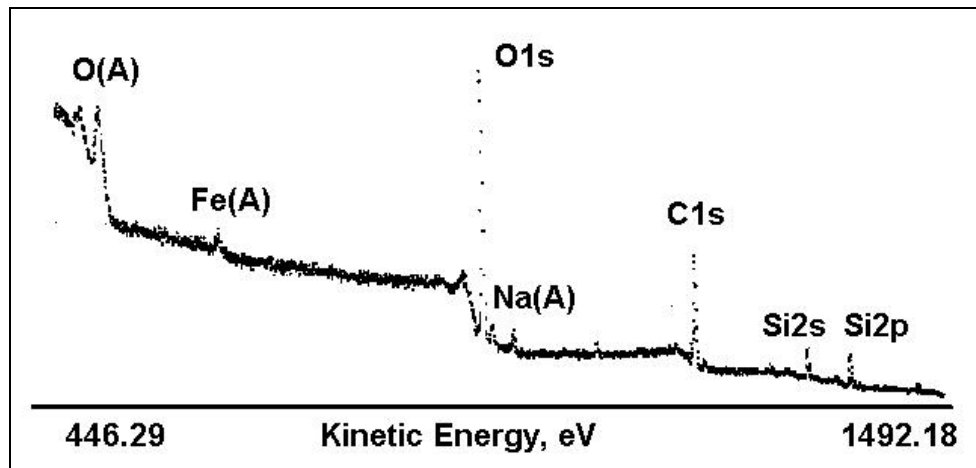
Figure 2. XPS survey spectrum of a rock sample.

The obtained spectra are fitted to separate the signals correspondent to the principal elements on the mineral surface. The positions of the main peaks are obtained after subtraction of the spectral signal from the base signal of the Al energy source of 1486.6 eV. In all cases a good fitting is found for the signals of the C-H, Si-C and Si-O of interest to this work, as shown in figures 3 and 4 respectively. For the C-H signal, the energy shift in the peak position (284.6 eV) for all the studied samples was less than 0.01 eV.
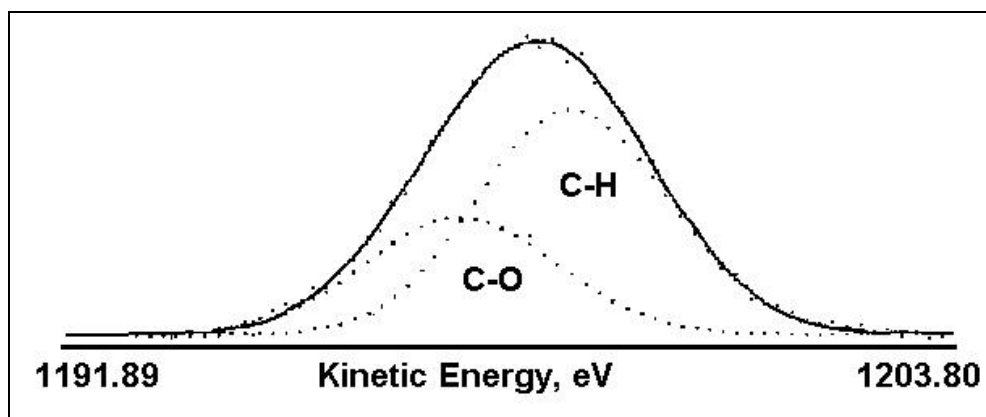
Figure 3. High-resolution XPS Carbon spectra.
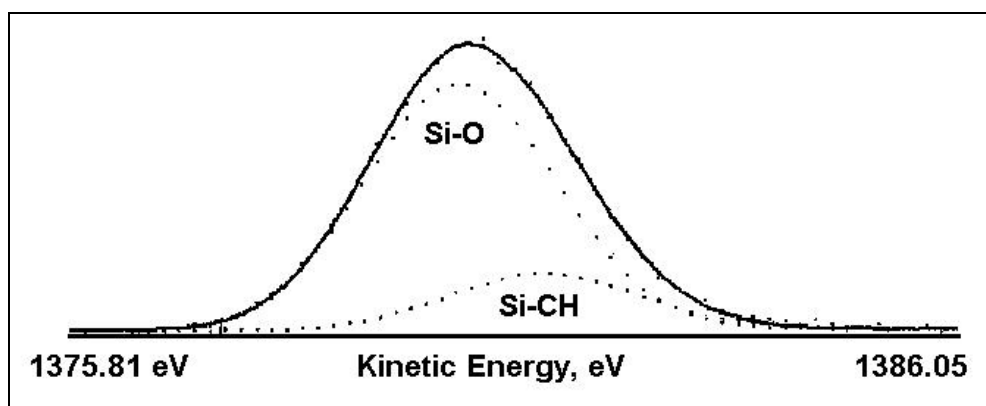
Figure 4. High-resolution XPS Silicon spectra.

As shown in Table 1, there is a non-zero energy shift in the Si signal for both the Si-H and Si-O cases, with main peaks at energy positions of 102.5 eV and 103.5 eV respectively. This energy shift has an average value of 0.204 eV for all the 132 samples analyzed in this work with a standard deviation of 0.04. In Table 1 we give the observed values of the energy shifts of a few of the samples as an example.

We have separated the samples in two groups according to the Si/O ratio value. One of the groups is composed of 66 samples with Si/O > 0.5 displaying oil affinity according to the conventional Amott-Harvey wettability index (Table 2). The second group with Si/O < 0.5 has 66 samples (Table 3).

From the sample set with Si/O > 0.5 (66 samples), it is found that 7 show differences in terms of the XPS prediction and the results form the Amott tests. Four (4) of those have values of C-H content in the boundary limits of the different wettability conditions, and three (3) present systematic deviations (samples B3, B10 and K5 in Table 2). In this case there is a 95.5 % of certainty in the prediction of both methods. All samples with Si/O

ratio > 0.5 show affinity to oil. These samples may present or not the signals correspondent to Si-CH and Si-O.

For the second group with Si/O ratio < 0.5 (66 samples), we have found differences between the XPS and the Amott test predictions in 10 samples, from which four (4) correspond to samples with a C-H content near the boundaries that separate different wettability regions. Five (5) samples are described as intermediate wet by XPS (E6, G2, G3, P3 and P6) analysis whereas the behavior according to the Amott-Harvey wettability index is neutrally wet. Also, five (5) of the samples are described as weakly water wet by XPS (B13, C2, C6, C9 and F10) and are neutral according to the Amott-Harvey index. This is a limitation of the XPS analysis since it can not distinguish samples with these conditions. However, excluding those cases the confidence range in using XPS data is of 91 % for these samples.

All the samples in the second group (Si/O ratio < 0.5) show a wetting condition ranging from intermediate wet to strongly water wet. There are samples such as D3, D4, F10, H7, I1, O1 and O2 that present the two Si signals (Si-CH and Si-O respectively). This result allows to claim that these signals are not determinant of the surface wetting condition.

CONCLUSIONS

The statistical analysis performed on 132 samples from different Venezuelan reservoirs confirms the validity of using XPS spectral data to describe the rock wetting condition with a high degree of confidence (above 91%). In all cases, it is required a good pre-processing of the survey spectra to properly fit the C-H, Si-CH and Si-O signals to Gaussian forms. The preliminary statistical analysis performed here supports the use of a faster quantitative technique such as the XPS spectroscopy to infer about important reservoir properties relevant to the oil recovery process.

NOMENCLATURE

at.	: atomic percentage
C-H	: atomic content of carbon singly bonded to an hydrogen atom (1s, 286.5 eV)
F	: fractional wetting condition
I	: intermediate wetting condition
N	: neutral wetting condition
OW	: strongly oil wet wettability condition
Si-CH	: atomic content of silicon singly bonded to a CH chain (2p, 102.5 eV)
Si-O	: atomic content of silicon singly bonded to an oxygen atom (2s, 103.5 eV)
Si/O	: ratio between Si and O content. Value for quartz is 0.5
V_{od}	: volume of oil by forced displacement
V_{osp}	: volume of oil spontaneously displaced
V_{wd}	: volume of water by forced displacement
V_{wsp}	: volume of water spontaneously displaced

WW   : strongly water wet wettability condition
WOW   weakly oil wettability condition
WWW   : weakly water wet condition
XPS   abbreviation of X-ray photoelectron spectroscopy
δ_n : neutral wetting index
δ_o : oil wetting index
δ_w : water wetting index
μ : fluid viscosity
ρ : fluid density

ACKNOWLEDGEMENTS

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Table 1. Energy shift in the silicon signal.

Sample	Si-CH (102.5 eV)	Energy Shift (eV)	Si-O (103.5)	Energy Shift (eV)
A1	18.13	0.4	-	-
A2	-	-	22.31	0.2
B1	6.08	0.1	-	-
B10	14.33	0.2	4.27	0.1
B14	13	0.6	-	-
B16	6.89	0.2	4.56	0.0
B17	6.77	0.0	4.36	0.3
D3	1.23	0.1	20.55	0.6
E5	8.43	0.2	4.36	0.3
E6	-	-	24.22	0.4
E7	10.37	0.0	8.11	0.1
F10	2.38	0.3	11.37	0.4
G3	18.98	0.4	-	-
H7	21.83	0.1	-	-
I1	15.93	0.2	-	-
S3	24.02	0.3	-	-
S4	-	-	25.93	0.0
S5	-	-	23.32	0.3
P1	-	-	19.7	0.3
P4	17.43	0.3	-	-
R3	16.53	0.3	-	-
R5	-	-	21.45	0.3
T1	10.27	0.4	4.57	0.2
V5	16.94	0.2	-	-
U1	12.84	0.2	-	-
X3	-	-	17.85	0.1

Table 2. C-H, Si-O and Si-CH content in samples with a Si/O > 0.5.

Sample	C-H (at. %) (284.6 eV)	Si-CH (at. %) (102.5 eV)	Si-O (at. %) (103.5)	Si/O	XPS	Amott-Harvey
A1	50.25	18.13	-	0.59	WOW	OW
B1	82.61	6.08	-	0.56	OW	OW
B2	61.65	3.26	-	0.57	OW	OW
B3	42.61	19.93	-	0.53	WOW	OW
B4	51.04	11.05	-	0.54	OW	OW
B5	44.55	10.27	3.25	0.55	WOW	WOW
B6	49.59	16.53	-	0.56	WOW	WOW
B7	47.87	13.11	2.45	0.54	WOW	WOW
B9	57.16	8.47	-	0.57	OW	OW
B10	44.25	14.33	4.27	0.53	WOW	OW
B11	41.35	10.23	5.28	0.54	WOW	WOW
B12	56.36	11.43	-	0.56	OW	OW
B14	60.19	13.00	-	0.58	OW	OW
B15	73.52	8.44	2.45	0.59	OW	OW
B16	76.19	6.89	4.56	0.59	OW	OW
B17	73.32	6.77	4.36	0.57	OW	OW
B18	74.65	5.23	5.89	0.58	OW	OW
B19	77.76	4.60	6.54	0.57	OW	OW
B20	73.94	8.84	3.78	0.56	OW	OW
B21	64.72	7.96	4.27	0.58	OW	OW
B22	65.27	5.56	5.23	0.57	OW	OW
D1	39.21	15.76	2.35	0.54	WOW	WOW
D2	42.46	10.15	4.37	0.55	WOW	WOW
D6	37.17	4.57	21.25	0.54	WOW	WOW
D7	36.71	-	24.94	0.52	WOW	WOW
E1	62.63	13.48	-	0.57	OW	OW
E2	57.26	15.36	-	0.55	OW	OW
E3	59.77	14.55	-	0.58	OW	OW
E4	53.76	13.79	-	0.57	OW	OW
E5	74.31	8.43	4.36	0.56	OW	OW
E7	74.18	10.37	8.11	0.59	OW	OW
H6	38.47	16.79	-	0.56	WOW	WOW
I2	53.25	14.66	-	0.57	OW	OW
I3	53.89	13.71	-	0.54	OW	OW
I4	47.07	15.45	-	0.51	WOW	WOW
I5	41.48	14.31	-	0.43	WOW	WOW
I6	50.98	13.94	-	0.52	OW	OW
I7	39.79	15.93	-	0.54	WOW	OW
I8	48.33	13.07	-	0.53	WOW	OW
J1	39.16	25.25	-	0.55	WOW	WOW
J2	39.75	23.68	-	0.54	WOW	WOW
J3	39.01	24.02	-	0.53	WOW	WOW
K2	50.96	13.67	-	0.58	OW	OW
K3	50.91	14.83	-	0.52	OW	OW

K4	51.56	14.10	-	0.51	OW	OW
K5	44.67	17.43	-	0.56	WOW	OW
L1	41.04	14.97	-	0.54	WOW	WOW
L2	51.74	11.74	-	0.56	OW	OW
L3	40.59	16.53	-	0.58	WOW	WOW
L4	37.64	21.58	-	0.63	WOW	WOW
L5	36.61	-	21.45	0.61	WOW	I
L6	44.01	19.86	-	0.63	WOW	WOW
L7	45.38	20.39	-	0.68	WOW	WOW
M1	53.85	15.62	-	0.59	OW	OW
M2	59.05	13.82	-	0.60	OW	OW
M3	51.48	15.20	-	0.53	OW	WOW
M4	45.07	16.80	-	0.52	WOW	WOW
M5	46.51	16.94	-	0.53	WOW	WOW
N1	63.01	12.84	-	0.61	OW	OW
N2	53.60	12.92	-	0.59	OW	OW
N3	51.50	13.77	-	0.51	OW	OW
N4	54.07	13.54	-	0.50	OW	OW
P1	38.82	16.09	-	0.55	WOW	WOW
P2	51.16	12.93	-	0.54	OW	WOW
P4	39.16	16.28	-	0.55	WOW	WOW
P5	39.30	16.12)	-	0.55	WOW	WOW

Table 3. C-H, Si-O and Si-CH content in samples with a Si/O < 0.5.

Sample	C-H at. (%) (284,6 eV)	Si-CH at. (%) (102,5 eV)	Si-O at. (%) (103,5)	Si/O	XPS	Amott-Harvey
A2	31,59	-	22,31	0,41	I	I
A3	30,72	-	21,64	0,42	I	I
A4	32,34	-	11,28	0,45	I	I
A5	20,90	-	18,56	0,40	WWW	WWW
A6	30,08	-	16,66	0,40	I	I
A7	21,48	-	18,77	0,39	WWW	N
A8	26,96	-	18,35	0,42	I	I
A9	24,07	-	18,95	0,43	WWW	WWW
A10	28,64	-	18,40	0,43	I	I
A11	15,98	-	20,85	0,42	WW	WW
A12	22,42	-	19,47	0,42	WWW	N
A13	26,31	-	18,60	0,43	I	I
A14	29,53	-	17,58	0,42	I	I
B8	36,35	-	18,24	0,42	I	I
B13	20,40	-	17,01	0,40	WWW	N
C1	7,66	-	24,35	0,40	WW	WW
C2	21,91	-	17,67	0,43	WWW	N
C3	15,79	-	21,24	0,42	WW	WW
C4	12,65	-	20,45	0,41	WW	WW
C5	18,93	-	16,26	0,42	WW	WW
C6	24,34	-	19,26	0,44	WWW	N

C7	17,27	-	20,34	0,41	WW	WW
C8	14,25	-	19,28	0,40	WW	WW
C9	19,56	-	18,46	0,46	WWW	N
C10	26,67	-	19,36	0,42	I	I
C11	25,58	-	20,49	0,41	I	I
C12	28,49	-	19,77	0,41	I	I
C13	20,45	-	17,35	0,43	WWW	WWW
C14	30,28	-	23,67	0,40	I	I
C15	12,67	-	18,39	0,38	WW	WW
D3	33,25	1,23	20,55	0,49	I	I
D4	28,67	1,38	19,98	0,45	I	I
D5	31,29	-	24,27	0,44	I	I
D8	27,57	-	19,86	0,44	I	I
D9	29,59	-	19,43	0,43	I	I
E6	31,24	-	24,22	0,44	I	N
F1	32,72	-	20,63	0,42	I	I
F2	32,48	-	21,28	0,45	I	I
F3	23,92	-	19,49	0,40	WWW	WWW
F4	30,06	-	19,67	0,43	I	I
F5	31,48	-	24,77	0,42	I	I
F6	28,93	-	21,35	0,42	I	I
F7	27,07	-	19,95	0,43	I	I
F8	28,64	-	18,40	0,43	I	I
F9	24,98	-	20,85	0,40	WWW	WWW
F10	21,32	2,38	11,37	0,43	WWW	N
F11	29,31	-	19,61	0,44	I	I
F12	34,53	-	18,58	0,42	I	I
G1	35,25	-	19,45	0,47	I	I
G2	28,67	18,98	-	0,44	I	N
G3	29,59	19,43	-	0,46	I	N
H1	15.17	-	27.35	0.44	WW	WW
H2	20.36	-	26.46	0.42	WWW	WWW
H3	20.13	-	25.01	0.40	WWW	WWW
H4	22.38	-	23.23	0.41	WWW	WWW
H5	18.36	-	25.95	0.45	WW	WW
H7	21,09	21,83	-	0,48	WWW	WWW
I1	31,79	15,93	-	0,44	I	I
J4	33,74	-	25,93	0,48	I	I
J5	28,88	-	23,32	0,49	I	I
J6	34,98	-	22,15	0,48	I	I
K1	36,33	-	19,70	0,48	I	I
O1	25,76	10,27	4,57	0,34	I	I
O2	30,52	2,71	6,79	0,37	I	I
P3	26,46	-	17,85	0,41	I	N
P6	35,85	-	15,71	0,42	I	N